The Institute of Paper Chemistry

Appleton, Wisconsin

Doctor's Dissertation

The Polarographic Reduction of Benzil Derivatives

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June, 1965

THE POLAROGRAPHIC REDUCTION OF BENZIL DERIVATIVES

A thesis submitted by

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June, 1965

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SUMMARY

The polarographic reduction of benzil has been studied by numerous investigators. The polarographic reduction of benzil derivatives has received little attention. Seven methoxy- and hydroxy-substituted benzil derivatives and benzil itself have been reduced in this investigation. Polarography and controlled potential electrolyses experiments were conducted in buffered 50% ethanol-water (by volume) solvent systems. The compounds were reduced in seven different buffered solutions over the "pH"* range 1.5 to 13.5.

At least one polarographic wave was produced by each of the compounds at all "pH's". There was also a second more negative wave at "pH's" 9 and higher. The first waves for all compounds were two-electron reductions at all the "pH's". The waves were not completely diffusion-controlled. The reductions were dependent upon the hydrogen-ion concentration. The dependence was different in the acidic than in the basic solutions. The reductions became more reversible as the "pH" increased, and benzil, m-anisil, and p-anisil were reduced reversibly in the very basic solutions. Kinetic analyses of the data indicated more than one irreversible process except for benzil, m-anisil, and p-anisil at "pH" 13.5.

Controlled potential electrolyses of benzil, p-anisil, and vanillil showed benzoin, p-anisoin, and vanilloin to be the reduction products of the first waves at all "pH's". However, polarographic reductions of benzoin, p-anisoin, and vanilloin indicated that the enediol form of the benzoin was the dropping mercury electrode reduction product. The enediol rearranges to the benzoin in a secondary reaction. This rearrangement is faster in basic than acidic media.

Electron-releasing substituents made the reductions more difficult (more negative half-wave potentials). Solvent-solute interactions such as hydrogen

*The pH values were measured in 50% ethanol-water and, therefore, are apparent pH values or "pH".

bonding and ionization, and also intramolecular hydrogen bonding in di- or tri-substituted compounds, complicated the reductions of the hydroxy-substituted compounds. These compounds were more irreversible than the nonhydroxy-substituted compounds. There is evidence that the ionized forms of the hydroxy-substituted compounds are reduced in the intermediate and very basic solutions.

A correlation between half-wave potentials and Hammett's sigma values was successful at "pH" 1.5 for all compounds except 3,3',4,4'-tetrahydroxybenzil. At higher "pH's" the correlation failed. However, a correlation was obtained with benzil, m-anisil, and p-anisil at all "pH's". This correlation was used to predict half-wave potentials of certain unsymmetrical benzils at "pH's" 1.5 and 13.5.

The reduction mechanism for benzil, m-anisil, and p-anisil is similar to that proposed by other investigators. A "pre-protonation" step in acidic media is proposed to explain the Hammett correlation at "pH" 1.5. At this "pH" the "pre-protonation" step is rate determining and offsets the solvent-solute interactions of the hydroxy-substituted compounds. At higher "pH's" these interactions become more important than "pre-protonation." As the "pH" is increased, the mechanism for hydroxy-substituted compounds is complicated by intermediate, irreversible steps caused by solvent and electric field interactions. However, the over-all reaction is the same for all compounds, since the same reduction products (benzoin and benzoin derivatives) were identified.

INTRODUCTION

Oxidation and reduction are two of the most important reactions used to study the structure and characteristics of organic compounds. Benzil and lignin "model" compounds such as vanillil, syringil, and 3,3',4,4'-tetrahydroxybenzil have been reduced by various chemical reducing agents (1-4).

The results from the chemical reduction of these compounds indicate that the substituents on the benzene rings influence the reduction of the 1,2-diketo group. For example, three different reducing agents were employed to prepare the benzoin-type reduction products of benzil, vanillil, and syringil. This indicates that the substituents are affecting the electron density around the diketo reduction site. However, chemical reduction affords only qualitative evidence of the effect of substituents on the reduction site.

Electrochemical methods have advantages over more conventional chemical techniques in studying the reaction mechanisms of organic compounds. Polarography and voltammetry give some evidence for the reactive intermediate in an electrochemical reaction. The effects of solvent, pH, temperature, and concentration of reducible species can be studied apart from the complicating effects of specific chemical reducing agents. The potential at which an electrochemical reaction occurs is a direct measure of molecular reactivity. Therefore, polarographic data can be used for quantitative correlations between reactivity and structure.

The Hammett equation (4a) is a quantitative relationship between structure and reactivity. Investigators have found correlations between the half-wave potentials of organic compounds and the Hammett substituent constants. A few of these investigations were with acetophenone, benzaldehyde, and their

derivatives (5, 6), substituted benzophenones (7, 8), and other less related series of substituted compounds (9, 10). Elving and Markowitz (11) have correlated half-wave potentials of substituted ethylenes with Taft's quantitative relationship for aliphatic compounds. These are but a few of the polarographic investigations correlating reactivity and structure.

The present study was undertaken to elucidate the electrochemical reduction mechanisms of benzil derivatives using the techniques of polarography and controlled potential electrolysis. Another objective of this study was to determine a quantitative relationship between reactivity and structure. The electrochemical experiments have been conducted in a 50% ethanol-water solvent over the "pH"* range of 1.5 to 13.5. Potentiometric titrations and ultraviolet spectra were obtained to help understand the ionization of hydroxy-substituted benzil derivatives and how the ionization affects the polarographic reductions. Benzoin and two benzoin derivatives were studied to help determine the reduction products. Benzil was studied in this investigation as a basis of comparison for a quantitative relationship. The benzil data also were useful for comparison with other investigations.

*The pH values were measured in 50% ethanol-water and, therefore, are apparent pH values or "pH".

LITERATURE REVIEW

Polarographic reduction of benzil, Ar·CO·CO·Ar, and of benzoin, Ar·CO·CH(OH)·Ar, has been described by many investigators (12-20, 23, 24). Adkins and Cox (12) observed two reduction waves for both benzil and benzoin. In alkaline solution the reduction potentials of both compounds coincided. Chodkowska and Grabowski (13) showed that the first wave is always due to reduction of benzil, which is easily formed in alkaline media by air oxidation of the enediol form of benzoin. The second wave is due to the reduction of benzoin. Gaglidardo (14) found the reduction wave of benzil to be concentration dependent in acid and neutral media. Bobrova and Tikhomirova (15) reported two waves for benzil as did Vityaeva and Markman (16). The solvent systems for the above investigations were different ratios of ethanol to water. The supporting electrolytes were lithium chloride, ammonium chloride, or one of the tetraalkylammonium salts. The above investigations were not in buffered solutions. Rogers and Kipnes (17) confirmed the suitability of anhydrous methanol as a solvent for the polarographic reduction of benzil.

A thorough study was done by Pasternak (18) who observed only one irreversible two-electron wave of benzil and of benzoin in a pH range of 1.2 to 11.3. Benzoin was isolated as the reduction product of controlled potential electrolyses at pH 1.3 and 8.6. However, he found stilbenediol to be the electrode product which slowly transformed to benzoin. Pasternak also showed that benzil forms complexes with borate buffer systems, one mole of benzil complexing with two moles of borate (19).

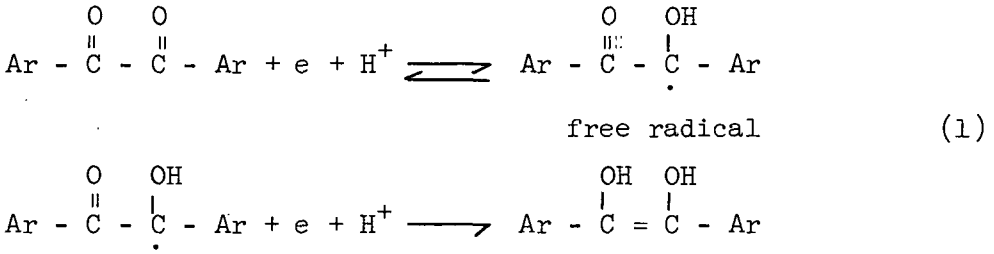
Kalvoda and Budnikov (20), using a.c. oscillographic polarography and a dropping mercury electrode, found the reduction of benzil proceeded to a radical which was reoxidized in the next a.c. half-period.

The polarographic reduction mechanisms of single carbonyl reduction sites, as found in acetophenone and benzophenone, have been investigated. Elving and Leone (21) have studied the reduction mechanisms of five alkyl phenyl ketones and benzophenone. They observed one diffusion-controlled pH-dependent and a more negative pH-independent wave in acidic media. These two waves merge into one around pH 6. At pH 9 and above a third more negative wave appeared. These waves were observed for all the above compounds. Suzuki and Elving (22) studied the kinetics and mechanisms for the electrochemical reduction of benzophenone in acidic media. The electron-transfer process of the first wave is quite rapid, but the subsequent irreversible chemical process of dimerization of the free radicals produced causes the net reaction to be irreversible. The process producing the second one-electron wave is quasi-reversible.

Recently attention has been given to the reduction of 1,2-diketones in order to understand the difference in the reduction of this functional group compared to single carbonyl reduction sites.

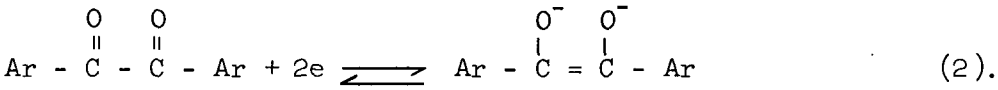
Philp, Flurry, and Day (23) studied the reduction of several diketones including benzil over the pH range 3 to 12 in ethanol-water media. They employed a switching technique to detect oxidizable intermediates. They observed an oxidizable intermediate over the pH range studied. The waves were irreversible in acidic media. In the pH range 9 to 10 there was a trend toward reversibility and at pH 12 a reversible wave was observed. They found no evidence for a change in mechanism over the pH range and reported a two-electron process as the potential-determining step in both acidic and basic media. Their experimental evidence did not clearly indicate the nature of the observed wave in the acidic media. From the fact that benzoin was the isolated product and the wave heights were identical in acidic media, they concluded that an enediol was formed and

was the species which produced the anodic current. They assumed the following stepwise process



free radical (1)

in which the second step is irreversible. In very basic media the following reversible two-electron process was proposed.



(2).

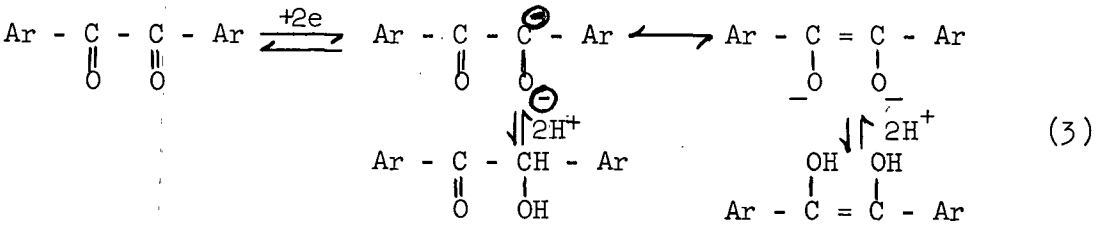
They also proposed a mechanism for the effect of acidity on the keto-enol equilibrium of the reduction product.

The reduction of benzil was studied in dimethylformamide (24). When tetrabutylammonium iodide was the supporting electrolyte, two one-electron waves were observed, and macroelectrolysis experiments definitely indicated the formation of a free radical. Electron paramagnetic resonance (EPR) showed the first wave to be reversible and the second irreversible. When lithium chloride was the supporting electrolyte, the authors could not distinguish between one 2-electron reversible wave or two 1-electron waves. They decided on the latter, assuming the lithium ion delocalized (by chelation) the charge of the first electron over the diketo reduction site and that the second electron transfer was too fast to be detected by EPR.

Chodkowska and Grabowski (13) studied the cathodic reduction of benzil at a dropping mercury electrode and with a stationary hanging mercury drop electrode using, in the latter case, a cyclic voltammetry technique. Their solvent system

was 48% ethanol by volume and they studied the pH range 3.6 to 14. Benzil formed a reduction product irreversibly in acid solutions but of growing reversibility with increasing pH. A second wave, absent in acid solutions, was present in alkaline solutions and was due to the reduction of benzoin which was formed indirectly as a final product of the first benzil reduction wave.

In strongly alkaline solutions, the reduction product of the reversible two-electron process of benzil was reoxidized reversibly at the stationary mercury electrode. They proposed the following scheme.

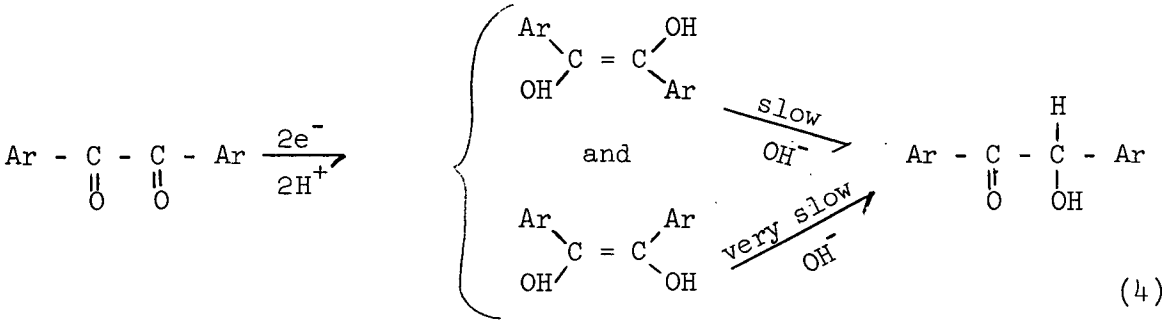


(3)

In acid and neutral solutions two products of the irreversible reduction of benzil were observed through their anodic oxidation currents at a stationary hanging mercury drop electrode. The two products were cis- and trans- stilbenediols. The cis- form is reoxidized at a higher overpotential* and transforms more slowly to benzoin than the trans- form. Therefore, the trans- stilbenediol is the favored reduction product. The trans to cis isomerization is very slow and does not compete with the trans-stilbenediol to benzoin tautomerization in homogeneous solution. They showed that the trans to cis isomerization is increased by a strong electric field such as that at the electrode. Partially polarized molecules can isomerize in a strong electric field with a lower activation energy than in the absence of the field. The cis/trans ratio increased with increasing negative voltage and a maximum was observed at -0.95 v. vs. a saturated calomel electrode. The decrease of the cis/trans ratio after -0.95 v. was attributed to desorption of the trans-stilbenediol reduction product. This product is

*Overpotential is defined on page 43.

squeezed out of the double layer by water molecules and the ions of the electrolyte, and the time of stay of the product is too short for the hindered rotation (trans- to cis-) to occur. The cis/trans ratio also increased with increasing temperature (1.3 to 23.5°C.), increasing pH (6.5 to 8.1, base catalysis), and was influenced by the cation of the supporting electrolyte. They proposed the following scheme for the reaction in acid and neutral media.



(4)

POLAROGRAPHY: THEORY AND ANALYSIS OF DATA

Basic definitions and the equations for polarographically reversible and irreversible waves are included in this section, as well as an explanation of the method of data analysis used in this investigation. The principles of polarography and controlled potential reduction have been described in detail by Kolthoff and Lingane (25), Delahay (26), and Meites (27).

The reduction potentials are negative corresponding to the European convention for reporting oxidation-reduction potentials. Cathodic currents are positive in accord with normal polarographic procedure. All potentials are measured vs. the saturated calomel electrode (s.c.e.) unless otherwise specified.

The plot of current (i) versus potential (E) is a polarogram. For any specified set of conditions (e.g., solvent, pH, temperature, ionic strength, and supporting electrolyte) there is a certain potential required for the reduction of the compound being studied. If the potential is below the decomposition potential* of the supporting electrolyte-solvent system, a sigmoid shaped curve is obtained which is called a polarographic wave. A wave is obtained for each reduction step of an electroactive species or for each electroactive species present if the reductions occur at potentials differing by approximately 0.15 volt or more. See Fig. 1.

As the applied potential is increased, the concentration of the electroactive species at the electrode surface decreases until it becomes nearly zero. Further increases in potential will result in no increase in current. The

*Potter (28) defines the decomposition potential as that potential at which an appreciable decomposition rate of the reactants takes place as indicated by the increased current flow. This potential has no well-defined theoretical significance, but is utilized in the operation of electrolytic processes.

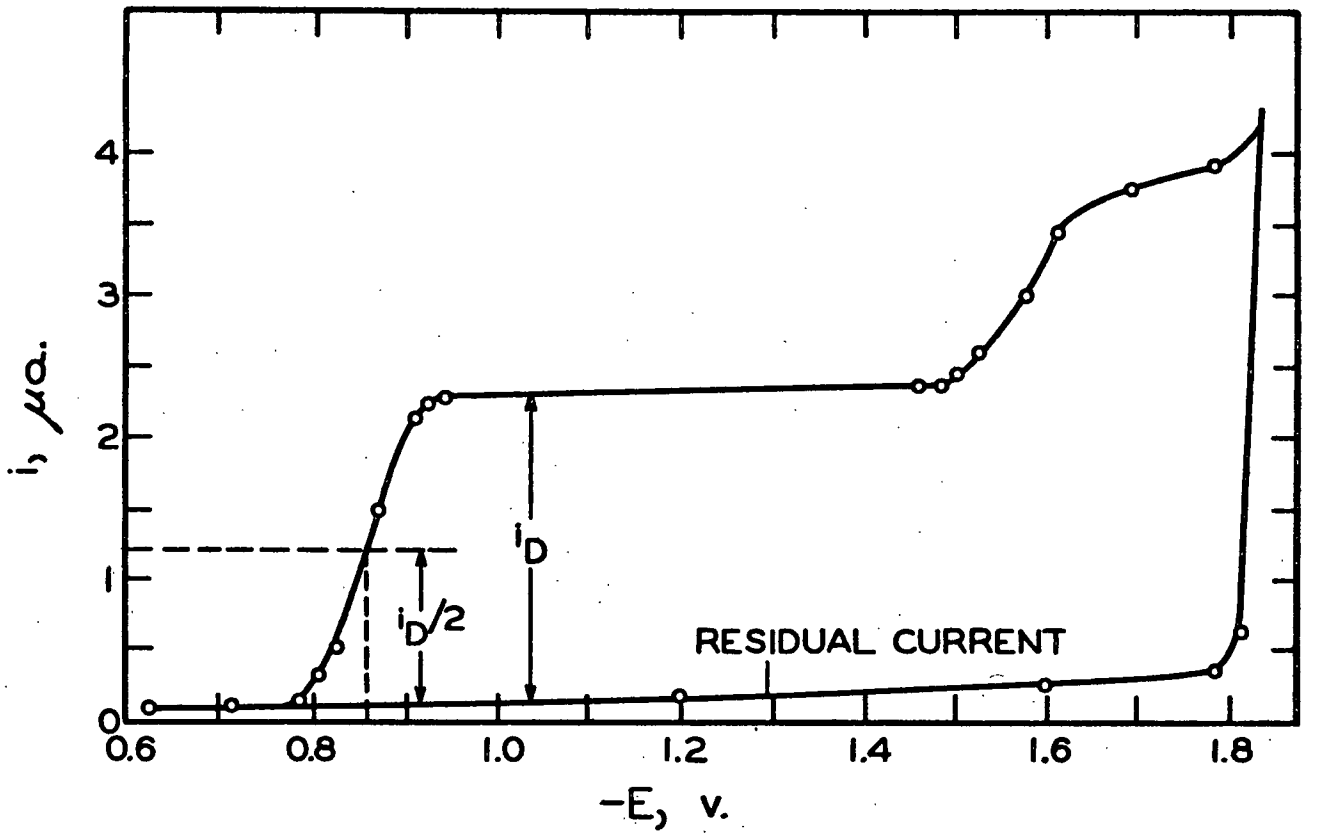


Figure 1. Polarogram of Benzil at 25.0°C. in 1:1 Ethanol:Water 0.06M KOH, and 0.14M KCl, "pH" 13.5

current level at this point is the limiting or diffusion current (i_D) and can be predicted by the Ilkovic Equation (6).

The residual current is the current obtained for the solvent-electrolyte system in the absence of the electroactive species being studied.

The potential corresponding to the current level midway between the diffusion current height and the residual current is called the half-wave potential ($E_{1/2}$).

The terminology and following equations are according to Delahay (26). A general equation for the electroreduction of an organic compound with hydrogen ion involved in the electrode process may be written

$$O + ne^- + mH^+ \underset{k_{b,h}}{\overset{k_{f,h}}{\rightleftharpoons}} R \qquad (5)$$

where O represents the species to be reduced and R represents the reduced species, n and m are the number of electrons and protons involved in the reaction, and $k_{f,h}$ and $k_{b,h}$ represent the heterogeneous rate constants for the reduction and oxidation, respectively. These are formal rate constants whereby concentrations instead of activities are used in the kinetic equations.

The current measured during the reduction of an electroactive species depends upon the kinetics of the electrochemical reaction and on the rate of mass transfer of the species involved in the electrode process. If the electrochemical reaction is so rapid that electrochemical equilibrium is achieved at the electrode at all times, the process is said to be polarographically "reversible" and the Nernst equation can be applied in the calculation of the electrode potential. This does not imply reversibility in the thermodynamic sense. Thus, when the heterogeneous rate constants are sufficiently large, the Ilkovic Equation (6) and the Heyrovsky-Ilkovic, Nernst-type Equation (7) apply. Equation (8) shows the factors which influence the half-wave potential. As shown, the $E_{1/2}$ is dependent upon the pH for a reversible electrode process.

$$i_D = 706\, n\, D_o^{1/2}\, C^o\, m^{2/3}\, t^{1/6} \qquad (6)$$

$$E = E_{1/2} - \frac{RT}{\alpha nF} \ln\left(\frac{i}{i_D - i}\right) \qquad (7)$$

$$E_{1/2} = E^o + z\,\frac{RT}{nF} \ln a_{H^+} - \frac{RT}{nF} \ln\left[\left(\frac{f_R}{f_o}\right)\left(\frac{D_o}{D_R}\right)^{1/2}\right] \qquad (8)$$

where

i_D = diffusion current, microamps (μa.)

n = number of electrons involved in the electrode process

$\underline{D_o}$ = diffusivity of the reducible species, sq. cm./sec.

$\underline{D_R}$ = diffusivity of the reduced species

$\underline{C^o}$ = concentration of the reducible species, in the bulk of the solution, m. mole/cc.

$\underline{m}$ = mass flow rate of mercury, mg./sec.

$\underline{t}$ = length of time that elapses between the instants at which two successive drops fall, sec.

α = transfer coefficient, or the fraction of the applied potential which favors the forward reaction

$\underline{E}$ = potential at any point on a polarographic wave referred to any arbitrary standard such as the s.c.e., volt

$\underline{E_{1/2}}$ = half-wave potential, volt

$\underline{R}$ = gas constant, 8.315 joules $(°K)^{-1}$ $(g.\text{-mole})^{-1}$

$\underline{T}$ = absolute temperature, °K .

$\underline{F}$ = Faraday constant, the number of international coulombs which must be passed through a cell to deposit one g. equivalent of any element, 96,500

$\underline{i}$ = current at any point on a polarographic wave, μa.

$\underline{E^o}$ = standard potential for the electrode reaction, volt

$\underline{z}$ = number of protons involved in the electrode process

$\underline{a_{H^+}}$ = activity of the hydrogen ion

$\underline{f_o}$ = activity coefficient of the reducible species

$\underline{f_R}$ = activity coefficient of the reduced species

The numerical factor 706, which includes the density of mercury, the Faraday, and a geometric factor, is used when the maximum current during drop life or the top oscillatory trace of a recorded polarogram is measured.

When the rate of the reverse reaction is sufficiently slow so that it can be neglected, the electrode reaction is said to be "totally irreversible." Equation (6) for the limiting current is still applicable, but Equations (7) and (8) are replaced by (9) and (10).

$$E = E_{1/2} - \frac{RT}{\alpha n_a F} \ln \left(\frac{i}{i_D - i} \right) \tag{9}$$

$$E_{1/2} = \frac{RT}{\alpha n_a F} \ln \left(\frac{k^o_{f,h}}{\lambda^{1/2} D_o^{1/2}} \right) + \frac{RT}{2\alpha n_a F} \ln t \tag{10}$$

where

α = transfer coefficient, or the fraction of the applied potential which favors the forward (reduction) process

n_a = number of electrons involved in the rate-determining or activation step

$k^o_{f,h}$ = rate constant for the reduction when E vs. a normal hydrogen electrode equals zero

$\lambda = k_{f,h}\, t^{1/2} / D_o^{1/2}$ and $\lambda_{1/2}$ is the value of $E_{1/2}$ and equals 0.76

It is interesting to note in Equation (10) that the half-wave potential for a totally irreversible wave is not directly dependent upon the pH although hydrogen ions are involved in the electrode process.

According to Delahay (29) the transition from reversible to totally irreversible waves occurs over a relatively narrow range of values of the rate constant. This is fortunate because in the intermediate range or "quasi reversible" range the theory is considerably more complex and not very well understood.

ANALYSIS OF DATA

Reversible polarographic waves or some irreversible polarographic waves have diffusion plateaus which have identical slopes as in the residual current curve, Fig. 1. In either of these circumstances the i_D is chosen as the height of the diffusion plateau and the $E_{1/2}$ is the potential at which the current level is $i_D/2$.

For many organic compounds irreversible waves are produced which have diffusion plateau slopes different from the slopes of the residual current curves, Fig. 2. In this case the selection of a diffusion current is an arbitrary matter.

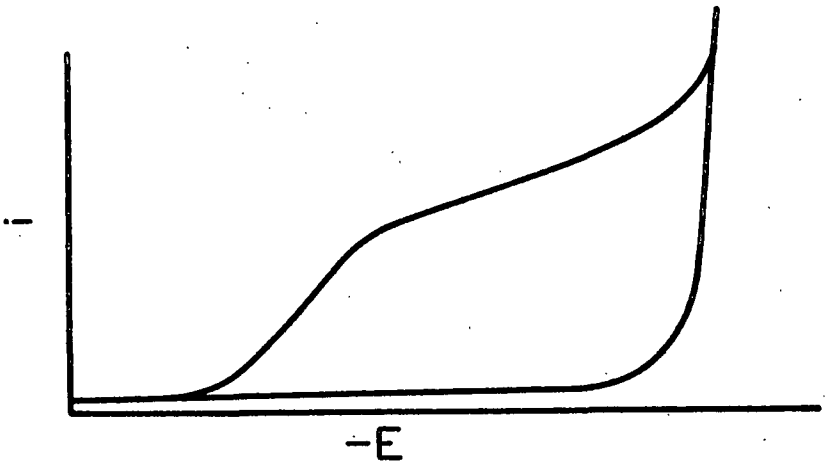


Figure 2. Irreversible Polarographic Wave

Some of the polarographic waves recorded during this investigation were reversible. Figure 1 shows the reversible wave for benzil at "pH" 13.5. Most of the polarographic waves were irreversible, and the more irreversible waves were shaped like the wave in Fig. 2.

Vermillion (30) developed a computer program (IBM 1620) for treatment of such voltammetric waves. This program was modified for the polarographic waves. A plot of the function $\ln (i/i_D - i)$ vs. E from Equation (7) should yield a straight line. From the slope of this line the value of n can be obtained. The $E_{1/2}$ can be determined from the intercept. By the use of a trial and error calculation i_D may be chosen as the current which gives the best least squares fit to a straight line in a plot of $\ln (i/i_D - i)$ vs. E.

Suzuki and Elving (22) have reported that the recorder for the Sargent Model XXI polarograph which has a full-scale balancing speed of 10 seconds was fast enough to make kinetic calculations from the recorded polarograms. Kinetic calculations are normally made from instantaneous currents recorded on very fast recorders (1 sec. balancing speed) or by oscillographic polarography. To verify the use of the Model XXI polarograph the above authors compared maximum recorder current values with those obtained from a cathode ray oscilloscope and found that the current values agreed within measuring error. The Sargent Model XV polarograph used in this investigation has a full-scale balancing speed of 10 seconds.

The polarograms recorded during this investigation were used to calculate rate constants by the Koutecky procedure as explained by Delahay (31). It has been shown that the ratio of the current at any potential to the diffusion current follows Equation (11).

$$\frac{i}{i_D} = \pi^{1/2} \lambda \exp(\lambda^2) \operatorname{erfc}(\lambda)^* \qquad (11)$$

where

$$\lambda = \frac{k_{f,h}\, t^{1/2}}{D_o^{1/2}} \qquad (12)$$

Koutecky has solved Equation (11) so that a value of λ is available for a value of i/i_D. The rate constant $k_{f,h}$ can then be calculated from Equation (12). The value $D_o^{1/2}$ was determined from the Ilkovic Equation (6), and $t^{1/2}$ is an experimentally measured value.

*The (erfc) equals [1-erf (λ)] where the notation erf(λ) represents the error integral defined by $\operatorname{erf}(\lambda) = 2/\pi^{1/2} \int_0^{\lambda} \exp(-z^2)\, dz$. Detailed tables of the function erf(λ) are available (32).

The rate constant $k_{f,h}$ is related to the potential by Equation (13).

$$k_{f,h} = k^{o}_{f,h} \exp \frac{-\alpha n_a FE}{RT} \qquad (13)$$

A plot of log $k_{f,h}$ vs. E should be a straight line if there is one and only one rate-determining process in the electrochemical reduction. The value of αn_a can be calculated from the slope, and the value of $k^{o}_{f,h}$ is determined from the intercept of the above plot when E equals zero vs. a normal hydrogen electrode. The values of αn_a and $k^{o}_{f,h}$ were then used to calculate the $E_{1/2}$ from Equation (10).

A computer program was developed to make the interpolations and needed calculations for the above kinetic study. The $E_{1/2}$ calculated from Equation (10) agreed within 5 millivolts with the $E_{1/2}$ determined from the intercept of the log $(i/i_D - i)$ vs. E plot. This is better than experimental error.

Although good correlation coefficients were obtained for the log $k_{f,h}$ vs. E* plots, the data did not produce straight lines when plotted. This fact will be discussed later.

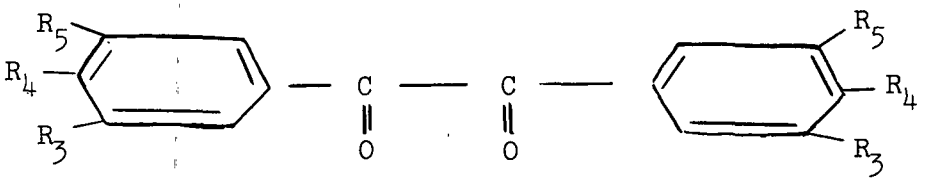
*The potential (E) is measured vs. a normal hydrogen electrode for use in Equation (13).

EXPERIMENTAL

CHEMICALS

Absolute ethanol was distilled in a column 22 mm. in diameter and 2.5 ft. long. The column was packed with glass tubing 6 mm. in diameter and 50 mm. in length. Water was purified by distilling from sodium hydroxide and potassium permanganate according to Weissberger (33). The water was polarographically pure after one distillation. The solvent system for the investigation was 50% ethanol-water (by volume).

Benzil (I) and the following benzil derivatives were reduced polarographically: m,m'-dimethoxybenzil or m-anisil (II); p,p'-dimethoxybenzil or p-anisil (III); m,m'-dihydroxybenzil (IV); p,p'-dihydroxybenzil (V); 3,3'-dimethoxy-4,4'-dihydroxybenzil or vanillil (VI); 3,3'5,5'-tetramethoxy-4,4'-dihydroxybenzil or syringil (VII); and 3,3',4,4'-tetrahydroxybenzil (VIII).



I. Benzil; $R_3 = R_4 = R_5 = H$

II. m-Anisil; $R_4 = R_5 = H$; $R_3 = CH_3O$

III. p-Anisil; $R_3 = R_5 = H$; $R_4 = CH_3O$

IV. m,m'-Dihydroxybenzil; $R_4 = R_5 = H$; $R_3 = OH$

V. p,p'-Dihydroxybenzil; $R_3 = R_5 = H$; $R_4 = OH$

VI. Vanillil; $R_5 = H$; $R_4 = H$; $R_3 = CH_3O$

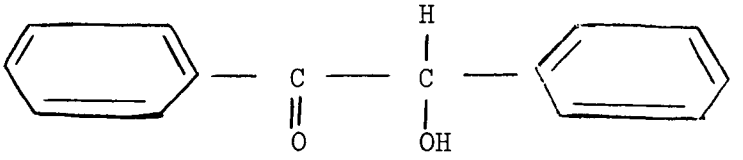
VII. Syringil; $R_3 = R_5 = CH_3O$; $R_4 = OH$

VIII. 3,3',4,4'-Tetrahydroxybenzil; $R_5 = H$; $R_3 = R_4 = OH$

IX. Veratril; $R_5 = H$; $R_3 = R_4 = CH_3O$

3,3',4,4'-Tetramethoxybenzil or veratril (IX) and p,p'-dichlorobenzil were not soluble at the appropriate concentration (0.5×10^{-3} M) in the 50% ethanol-water solvent system and, therefore, were not studied.

Benzoin (X) and the following benzoin derivatives also were studied: p-anisoin, syringoin, and vanilloin.



X

The following benzaldehyde derivatives were studied for comparison with the benzil derivatives: m-hydroxybenzaldehyde, p-hydroxybenzaldehyde, syringaldehyde, 3,4-dihydroxybenzaldehyde, and vanillin.

Most of these compounds were obtained from the library of chemical compounds of the Lignin Group at The Institute of Paper Chemistry. Others were synthesized and some were purchased. The compounds used, their origin and their purification, are included in Table I.

All compounds used for preparing buffer solutions and as supporting electrolytes were Analytical Reagent grade. Buffer solutions were prepared in a 50% ethanol-water solvent system. The "pH" of each solution was measured with a Beckman Model M glass electrode pH meter using a Beckman E-2 glass electrode. This "pH" is termed an apparent pH since the solvent system is not 100% water. Throughout this thesis the apparent pH will be designated as "pH". The same buffer solutions were prepared in 100% water and the pH measured. The buffer components, the apparent pH ("pH"), the pH in 100% water, and the resistance of

TABLE I

ORGANIC COMPOUNDS

Compound	Recrystn. Solvent	M.P. After Recrystn., °C.[a]	Reported M.P., °C.[a]	Origin	Ref.
Benzil	95% Ethanol	95-95.5	95	P[b]	(34)
p-Anisil	95% Ethanol	132-132.5	133	P	(35)
m-Anisil	60% Ethanol	83	83	Syn.[c]	(36)
m,m'-Dihydroxybenzil	Water	149-150	149-149.5	Syn.	(37)
p,p'-Dihydroxybenzil	Water	246-249	245-247	Syn.	(37)
Syringil	95% Ethanol	199-200	198	Lib.[d]	(3)
3,3',4,4'-Tetrahydroxybenzil	Water	235-237	234-236	Lib.	(4)
Vanillil	Acetic acid	232-233.5	233-234	Lib.	(2)
Benzoin	95% Ethanol	135.5-136	137	P	(1)
p-Anisoin	95% Ethanol	111-112	113	P	(38)
Syringoin	--[e]	165-167	165-166	Lib.	(3)
Vanilloin	95% Ethanol	159-161	161-162	Lib.	(39)
m-Hydroxybenzaldehyde	Water	103-104	101-103	P	(40)
p-Hydroxybenzaldehyde	--[e]	117-118	116	P	(41)
Syringaldehyde	--[e]	112-113	110	Lib.	(3)
3,4-Dihydroxybenzaldehyde	Toluene[e]	153.5-155	151-152	Lib.	(42)
Vanillin	--[e]	82-83.5	81-82	P	(43)

[a] All melting points are uncorrected. A Thomas-Hoover Capillary Melting Point Apparatus was used.

[b] Purchased from Distillation Products Industries, Eastman Kodak Co., and K and K Laboratories.

[c] Prepared during this work using the method indicated.

[d] Obtained from the library of chemical compounds of the Lignin Group at The Institute of Paper Chemistry. Originally prepared by Pearl, et al.

[e] Not recrystallized.

the polarographic cell containing the buffer solutions are shown in Table II. The least concentrated component of the buffer system was at least 120 times the concentration of the reducible species. This concentration is in agreement with Elving's (44) suggestion of 100 to 500 times the concentration of reducible species for organic polarography. Meites (45) suggests a minimum buffer concentration of 20 times the concentration of reducible species. Potassium chloride was used to adjust the ionic strength to 0.2 for all buffers except the potassium carbonate-hydrochloric acid buffer, which had an ionic strength of 0.42.

The purity of the buffer solutions was determined by recording residual current curves (no reducible-organic species present). In all cases a smooth curve was obtained at the desired current sensitivity.

The choice of buffers was very limited in the alkaline region. The borate system could not be used because it forms a complex with benzil (19). Phosphate buffer, at the desired concentration, formed an immiscible layer in the 50% ethanol-aqueous solvent system. These buffers could only be used if the concentration of buffer was decreased, or if the solvent system was changed. Neither of these alternatives was desirable. The carbonate system used at "pH" 11.30 proved to be a poor buffer. The equilibration rate was apparently too slow compared to the electrochemical reduction. Also, only monovalent buffer components could be used if an ionic strength of 0.2, as suggested by Meites (46), was to be maintained. These facts made it very hard to study the "pH" region between 9 and 13.

APPARATUS

A Sargent Model XV recording polarograph and a Sargent Model A IR compensator were used in this investigation. The polarograph was standardized with a potentiometer and no correction to the applied voltage was necessary.

TABLE II

BUFFER SOLUTIONS

Buffer Component	Apparent pH	pH in 100% Water	Cell Resistance,[a] ohms
NaOAc HCl KCl	1.55	1.20	410 550
NaOAc HCl (concd.) KCl	3.00	2.72	550 850
NaOAc HAc (concd.) KCl	5.10	4.18	500 750
$(C_2H_5)_3$ N HCl (concd.) KCl	7.20	7.50	495 610
NH_4Cl NH_4OH KCl	8.90	9.21	470 650
K_2CO_3[b] HCl (concd.)	11.30	9.90	430 610
KOH KCl	13.50	12.60	340 560

[a] Two saturated calomel electrodes were used with the polarographic cell. The two cell resistances are for each of the cells composed of one of these electrodes and a platinum electrode.

[b] Carbonate buffers (44) have been found to attain equilibrium too slowly compared with the electrode reaction.

The polarographic cell assembly described by O'Connor (47) was used in this study with two modifications. A second saturated calomel electrode was added so that the polarograms could be corrected automatically for the internal cell resistance or IR drop across the cell. A dropping mercury electrode instead of a platinum wire electrode was used.

The 40-ml. capacity cathode compartment and the two saturated calomel reference electrode compartments were water-jacketed and maintained at 25.0 ± 0.05°C. with water from a constant temperature bath. Glass cylinders with grade medium frits isolated the agar bridges of the saturated calomel electrodes from the test solution. This prevented contamination of the test solution by excessive water and chloride ion.

Prepurified nitrogen (Matheson) was used for deaeration of the test solutions. It was passed through two presaturation tubes containing 50% ethanol-water solvent which were kept in the constant temperature bath. The nitrogen could be directed by means of a two-way stopcock either into a dispersion tube immersed in the test solution or over the surface of the test solution while recording polarograms.

The saturated calomel half cells used in this investigation were prepared as suggested by Meites (48). The tip of the agar bridge was kept immersed in a saturated potassium chloride solution when not in use. This kept the agar bridge in good condition and the cell resistance did not increase by more than 150 ohms throughout this study.

A Sargent (S-29417) 21-cm. capillary was used as the dropping mercury electrode (DME). The drop time (t) and mercury flow rate (m) were 6 sec. and 1.636 mg./sec., respectively, with an open circuit and a mercury height of 62.5 cm.

The effect of potential on the drop time and product $\underline{m}^{2/3}\ \underline{t}^{1/6}$ is shown in Fig. 3. The variation of ($\underline{m}$) with potential was only 0.008 mg./sec. from 0 to -1.5 volt. Therefore, the product $\underline{m}^{2/3}\ \underline{t}^{1/6}$ curve was less potential dependent than ($\underline{t}$).

Controlled potential electrolyses were carried out using an Analytical Instruments Inc. Potentiostat. A Sargent Recording Potentiometer (S-72150) on a current range was used to record current-time curves which could be integrated for coulometric data. The potential output of the Potentiostat was determined by means of a Leeds and Northrup Student Potentiometer before and during the electrolyses. Contrary to the statement of the manufacturer (49), it was necessary to make periodic adjustments of the gain control in the amplifier chassis to get a close degree of potential control during the electrolyses.

A double-diaphragm cell with a cylindrical working electrode compartment (300-ml. capacity) was used as the electrolysis cell. This cell is recommended for use with the above Potentiostat and is manufactured by Analytical Instruments Inc. (49). The working electrode compartment was fitted with a one-hole Teflon cap through which a glass stirring rod was inserted. A stirred mercury pool, area 38.5 sq. cm., was the working electrode. A Beckman 5-inch fiber-junction saturated calomel reference electrode and a 1/8-inch carbon rod auxiliary electrode completed the cell assembly.

Resistance measurements were made with a General Radio Company Type 650-A Impedance Bridge containing a 1000 cycle/sec. a.c. current source. A Heathkit Extended Range Oscilloscope served as a null detector. The polarographic cell resistances are shown in Table II.

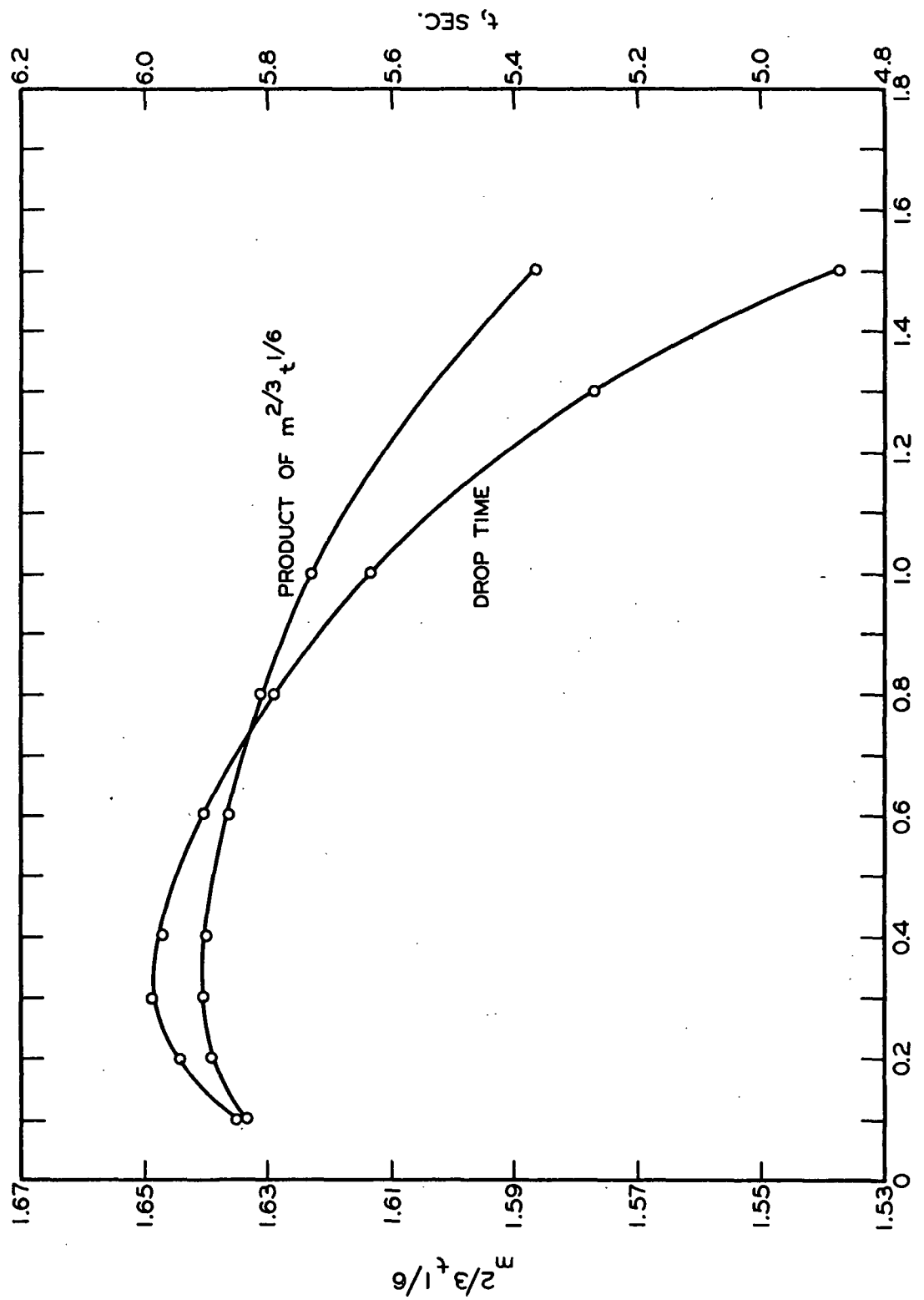


Figure 3. Capillary Characteristics Curves; Effect of Potential on Drop Time and Mercury Flow Rate (Determined in "pH" 9 Buffer System)

Ultraviolet curves were obtained with a Beckman Model DK2 spectrophotometer. Infrared curves were run on a Perkin-Elmer Model 21 spectrophotometer. A Wilkens Aerograph Model A-700 "Autoprep" gas chromatograph was used for identification of products. All weighings were made on an analytical balance.

POLAROGRAPHIC PROCEDURE

Stock solutions of 0.01M organic compounds in purified absolute ethanol were prepared and used for two days only. These stock solutions were found to be unstable after 10 days. The first polarographic wave of an aged benzil solution decreased in height and a new wave appeared at all "pH's". The half-wave potential of the new wave was more than that of the first wave but less than that of the second wave in alkaline media. The residue from evaporation of an aged benzil solution had an odor similar to ethyl benzoate. An aged ethanol solution of benzil or p-anisil consumed alkali during a potentiometric titration. The shape of a ml. vs. "pH" plot was not the same as a blank titration. A water-soluble substance, m.p. 111-113°C., was isolated after the potentiometric titration of an aged benzil solution. A fresh ethanol solution of benzil or p-anisil produced a ml. vs. "pH" plot very similar to the blank titration. Doering and Urban (50) isolated benzilic acid (7%), benzoic acid (36%), ethyl benzoate (10%), and ethyl dibenzoin (3%) from a dried ethanol solution of benzil and sodium ethoxide after it stood for 5 days. The percentage of benzilic acid increased when water was present. The rearrangement in my study occurred in 100% ethanol. The nature of the rearrangement and the products formed were not further studied. The products could be similar to those reported by Doering and Urban. Chodkowska and Grabowski (13) also have reported that benzil slowly disappears in an irreversible reaction in dilute alkaline solutions.

Thirty-six milliliters of a buffer solution, 2 ml. of water, and 2 ml. of a stock organic solution were pipetted into the cell and deaerated for 30 minutes with nitrogen. The concentration of reducible species was always 0.0005M unless otherwise specified. The glass cylinders were filled with the test solution and the electrodes introduced into the cell.

Polarograms were recorded at two polarization rates, 0.2 and 0.1 volt per min. for the more easily reduced compounds; 0.2 and 0.3 volt per min. for the less easily reduced compounds. The polarograms showed no significant change with polarization rate or with direction of applied voltage (0 to -2 vs. -2 to 0). All polarograms were recorded at a current sensitivity of 0.030 microamps (μa.) per mm. unless otherwise specified. The correction for internal resistance at this sensitivity was small and could be neglected. All polarograms were recorded without damping. At least four duplicate polarograms were recorded for each compound at each "pH", and the reported data are averages of the four polarograms. The top oscillatory traces of the waves were used to measure the current.

ELECTROLYSES AND ISOLATION PROCEDURES AND RESULTS

The controlled potential electrolyses conditions were determined from the polarographic data. Potentials on the diffusion plateaus of the polarograms were chosen as the electrolyses potentials. The concentration of reducible species was always 0.0005M.

The auxiliary electrode compartment and the middle section of the electrolysis cell were filled with 50 and 30 ml., respectively, of the desired buffer solution. Thirty-five milliliters of mercury (cleaned), 180 ml. buffer solution, and 10 ml. water were added to the working electrode compartment and deaerated for 30 minutes with nitrogen. This solution was pre-electrolyzed at a potential

0.3 to 0.4 volt more negative than the desired electrolysis potential until a constant current was obtained. Then 10 ml. of a 0.01M organic solution was introduced into the working electrode compartment and deaerated for 15 minutes. The electrolysis was commenced and continued until a constant current was obtained, usually about 1 to 3% of the initial current. This indicates a 97 to 99% reduction. The electrolyses times varied from 2 to 3-1/2 hours, the electrolyses at the lower "pH's" requiring the longer times.

The number of electrons (n) involved in the reduction was calculated from the current-time recordings by integrating with a planimeter. The value of (n) was always greater than 2, but less than 2.5, indicating a 2-electron reduction. The variation of (n) was due to experimental error since only the two-electron reduction products such as benzoin, p-anisoin, and vanilloin were identified.

The reduction products were isolated from the inorganic buffer salts of the electrolyses solutions by the following procedure:

1. The ethanol was evaporated at reduced pressure on a rotary evaporator. The concentration of inorganic material was kept small by addition of water.
2. The more basic buffers were acidified with dilute acetic or hydrochloric acid since some of the reduction products are soluble in alkaline solution.
3. The aqueous solution was extracted with ether.
4. The ether solution was dried over anhydrous magnesium sulfate and reduced in volume.
5. The dried ether solution was evaporated to dryness in a vacuum desiccator.

Blank experiments, using benzoin and p-anisoin, showed that the anhydrous magnesium sulfate had no effect on the organic material. Based on these results quantitative isolation of all products is assumed.

The number of reduction products was determined by thin layer chromatography (TLC) and gas chromatography after Step 4. The electrolyses of benzil at "pH's" 3, 5, 7.2, 9, and 11.3 contained one product. These products were identified as benzoin by infrared spectra and mixed melting points. The electrolyses of benzil at "pH's" 1.5 and 13.5, and p-anisil and vanillil at all "pH's" contained two products. TLC showed that one product had the same R_f and color reactions as the starting material (benzil, p-anisil, or vanillil). The other product had the same R_f and color reactions as the expected reduction product (benzoin, p-anisoin, or vanilloin). Gas chromatography also was used to identify benzoin as the reduction products of benzil electrolyses at "pH's" 1.5 and 13.5, and to identify p-anisoin as the reduction product of p-anisil electrolyses at all "pH's".

Blank isolations of authentic p-anisoin and vanilloin from all buffer solutions contained p-anisil and vanillil, respectively. Blank isolations of authentic benzoin from "pH" 1.5 and 13.5 buffer solutions contained benzil. The enolization of many ketones is catalyzed by both acids and bases. The presence of substituent groups also affects the keto-enol equilibria although the effects are not always in the same direction, as pointed out by Gould (51). The enediols are sensitive to oxidizing agents and are rapidly oxidized to benzil on exposure to air (52). These reasons suggest that the enediols of benzoin, p-anisoin, and vanilloin are oxidized to benzil, p-anisil, and vanillil during the isolation procedure.

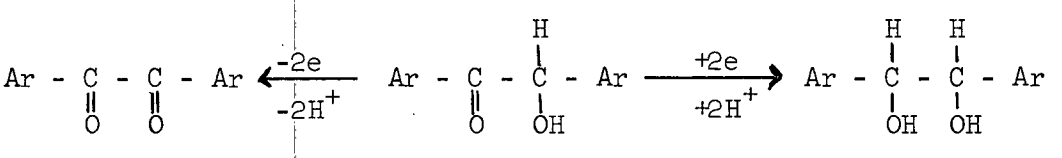
Silica Gel G purchased from the Microchemical Specialties Company was used as the TLC adsorbent. Benzil-benzoin separation was complete when the thin layer plates were developed first with 100% low boiling petroleum ether (35-60°C.). After drying, the plate was developed with 19:1 petroleum ether:absolute ethanol. p-Anisil and p-anisoin separation was complete using 100% chloroform as the

developing solvent. A trace of glacial acetic acid (0.5%) in the above solvents minimized streaking. No solvent system was found which completely separated vanillil from vanilloin. However, a 7:3 toluene:ethyl acetate developer with a trace of glacial acetic acid produced enough separation for identification. Sulfuric acid (50%) and 2,4-dinitrophenylhydrazine were used to spray the plates.

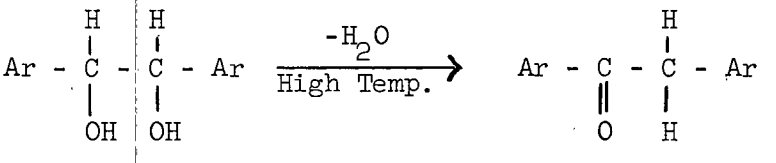
A Wilkens, 3/8-inch x 20-ft. aluminum column packed with 30% SE-30 (type of silicone rubber) on 45/60 mesh Chromosorb W was used for gas chromatography. The column temperature was 300 to 315°C. The ether solutions from the electrolyses of p-anisil at all "pH's" and benzil at "pH's" 1.5 and 13.5 produced two maxima when injected into the gas chromatograph. Authentic benzoin and p-anisoin each produced two maxima. The materials from these maxima were collected and identified as benzil and deoxybenzoin, and p-anisil and p-deoxyanisoin, respectively.

Gas chromatography of hydrobenzoin produced one peak corresponding to the peak identified for deoxybenzoin. Gas chromatography of a mixture of benzil, benzoin, deoxybenzoin, and hydrobenzoin produced two peaks corresponding to the peaks identified for benzil and deoxybenzoin.

Evidently benzoin disproportionates to benzil and hydrobenzoin. The column temperature would facilitate the splitting of water from hydrobenzoin to form deoxybenzoin.



Benzil Benzoin Hydrobenzoin



Deoxybenzoin

The same mechanism is proposed for p-anisoin.

Gas chromatography of vanillil and vanilloin produced no peaks. These compounds were refluxed with hexamethyldisilazane and trimethylchlorosilane in pyridine for one hour according to Freedman and Croitoru (53) in an attempt to prepare the trimethylsilyl (TMS) derivative. This reaction mixture, originally containing vanillil and vanilloin, was injected into the gas chromatograph and two peaks were observed.

A reaction mixture of TMS and p-anisoin produced a peak different than the original two peaks of p-anisoin. The material from this peak was collected, and an infrared spectrum had a carbonyl band, stronger CH bands than p-anisoin, and bands similar to silicone at lower frequencies (1200 and less). Based on these data it is assumed a complex of p-anisoin and TMS was made.

POTENTIOMETRIC TITRATION PROCEDURE AND RESULTS

The concentration of titratable species was 0.005M unless otherwise specified. Twenty milliliters of the 0.01M stock solution of organic compound and 20 ml. of water were pipetted into a beaker. The beaker was covered with "parafilm" through which an eyedropper was inserted for deaerating the solution with presaturated nitrogen. The solution was deaerated for 30 minutes and the nitrogen was bubbled through the solution during the titration to provide mixing. The pH meter electrodes and a buret were inserted through the "parafilm." The initial "pH" was measured and then small increments of sodium or potassium hydroxide were added and the "pH" recorded. The titrant was dissolved in 1:1 ethanol-water and also was deaerated before addition. The titrant was standardized with hydrochloric acid and was 0.016 or 0.008N for most titrations. The "pH" was measured 2 to 4 min. after each titrant addition to assure equilibrium conditions.

Blank titrations were made with 40 ml. of 1:1 ethanol-water and 20 ml. of ethanol. The potentiometric titrations were reproducible to 0.025 "pH" unit.

Table III shows the results of the titrations of the hydroxy-substituted benzils and the corresponding hydroxy-substituted benzaldehydes. Figures 4 and 5 are "pH" vs. ml. plots.

TABLE III

POTENTIOMETRIC TITRATIONS

Compound	Initial "pH"	"pH" of Max. Inflec. Pt.	Alkali[a,b] Consumed at Max. Inflec. Pt., equiv. x 10^4	Alkali[c] Consumed to Attain "pH" 8, equiv. x 10^4
p-Anisil	6.91	--	--	0.006
Benzil	5.90	--	--	0.012
m,m'-Dihydroxybenzil	6.03	11.31	4.128	0.049
Syringil	6.09	11.09	4.131	0.729
Vanillil	5.72	10.62	4.027	1.345
p,p'-Dihydroxybenzil	5.50	10.60	3.961	1.320
3,3',4,4'-Tetrahydroxybenzil	5.23	10.49	4.006	1.678
m-Hydroxybenzaldehyde	7.29	11.40	1.943	0.014
Syringaldehyde	6.60	10.56	2.014	0.400
Vanillin	6.10	10.37	2.009	0.493
p-Hydroxybenzaldehyde	6.11	10.50	2.027	0.410
3,4-Dihydroxybenzaldehyde	5.85	10.29	1.959	0.659

[a]Using a conversion factor of 2 equiv./mole, there was 4×10^{-4} equivalent of organic material present during the titration of the benzil derivatives. Using 1 equiv./mole as the conversion factor, there was 2×10^{-4} equivalent of organic material present during the titration of the benzaldehyde derivatives.

[b]All results are corrected for the blank titration.

[c]The initial "pH" of 40 ml. of 1:1 ethanol-water was 8.00.

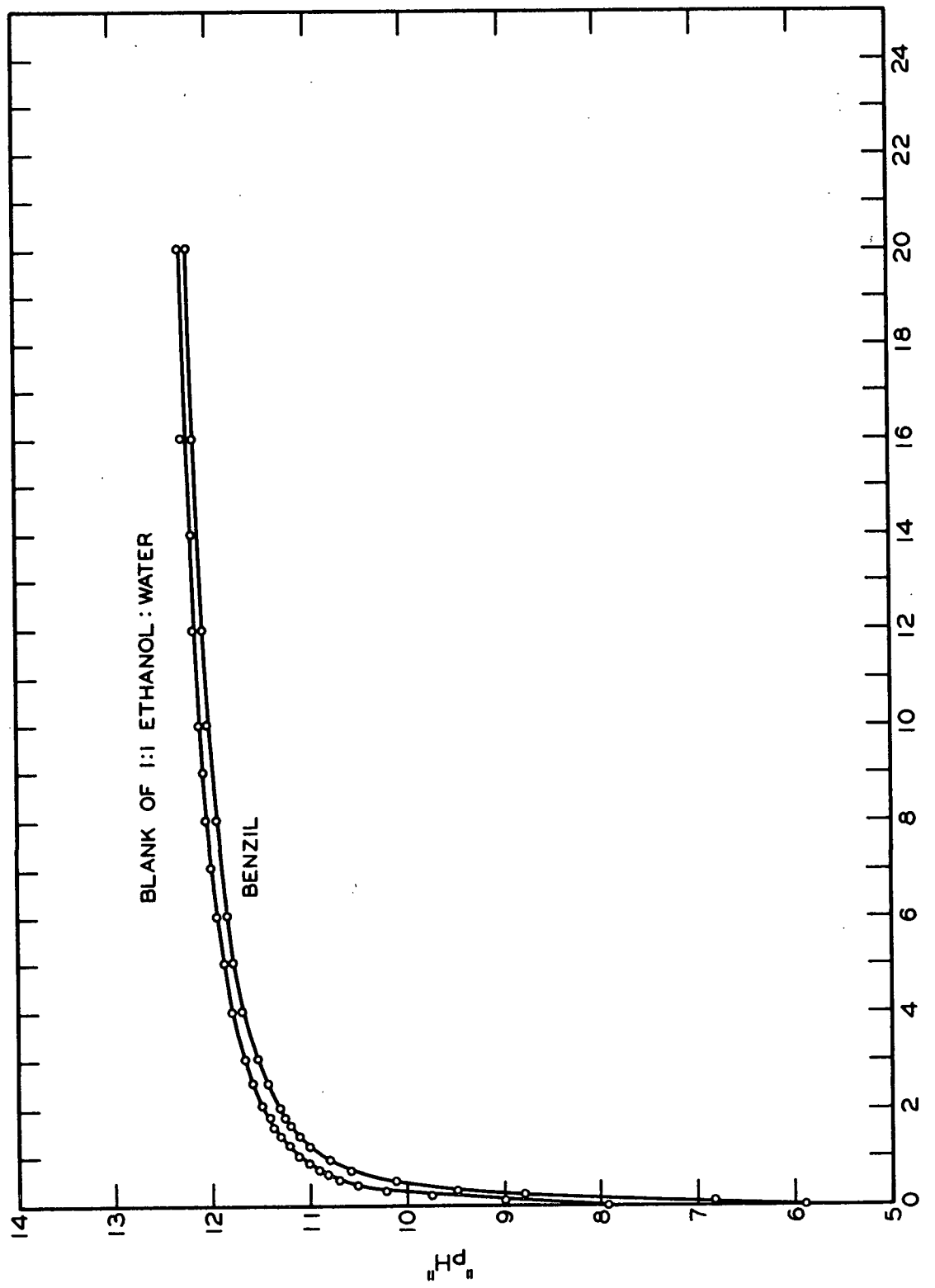


Figure 4. Potentiometric Titration of Benzil and a 1:1 Ethanol:Water Blank with 0.008N KOH

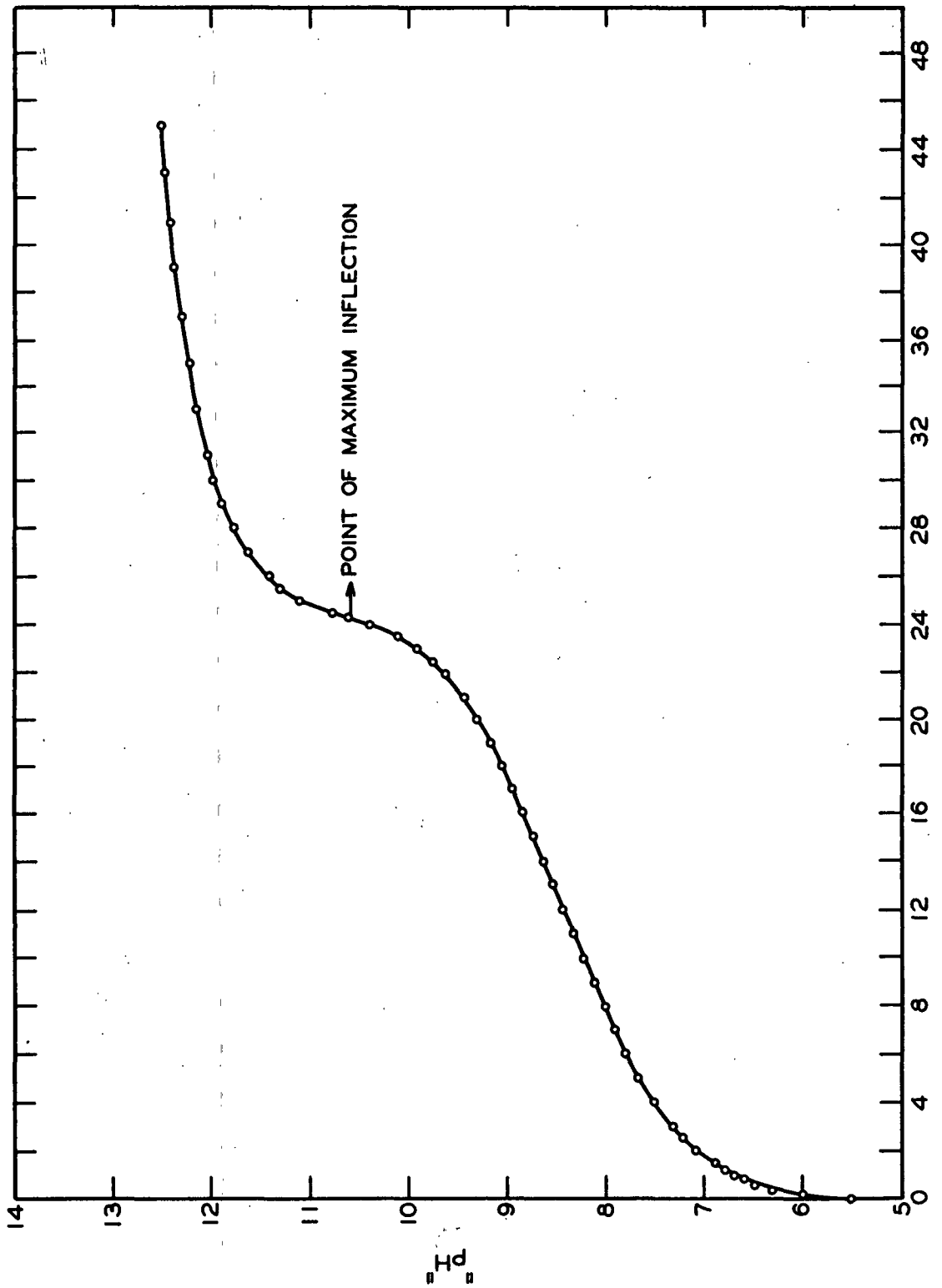
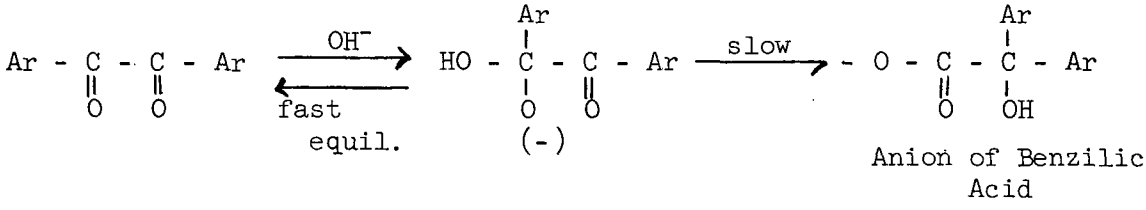


Figure 5. Potentiometric Titration of p,p'-Dihydroxybenzil with 0.0164N KOH

Figure 4 shows 0.564×10^{-4} equivalents (7 ml.) alkali were consumed by the blank to obtain "pH" 12.00. An ethanol blank required only 0.3 ml. to obtain the same "pH". Evidently, the ionization of water causes the extra alkali consumption and the shape of the curve.

The small alkali consumption of benzil and p-anisil could be due to the benzilic acid rearrangement (54).



The ml. vs. "pH" curve for p,p'-dihydroxybenzil (Fig. 5) is typical for all the hydroxy-substituted benzils. Only one inflection is apparent and at the maximum inflection point two equivalents of alkali per mole of p,p'-dihydroxybenzil are consumed. This indicates that both the hydroxyl substituents are ionized at this point. The absence of an inflection after the addition of 12 ml. of alkali indicates a gradual ionization from a nonionized to a divalent species. The monovalent species is probably present as an intermediate species. It should be noted that the initial increase of "pH" from 5.5 to 7.5 of Fig. 5 is caused by the solvent system.

ULTRAVIOLET SPECTRA PROCEDURE AND RESULTS

The concentration of the hydroxy-substituted benzils was 8 mg. per liter. The concentration of hydroxy-substituted benzaldehydes was 4 mg. per liter. A microsyringe was used to add the organic compound (from a 0.01M stock solution) to a 50-ml. volumetric flask containing a buffer solution. The solutions were prepared the same day the ultraviolet spectra were recorded.

p,p'-Dihydroxybenzil at "pH" 11.3 and p-hydroxybenzaldehyde over the "pH" range 7.2 to 13.5 obeyed Beer's law within experimental error of solution preparation and instrumentation.

The wavelengths and molar absorptivities of the hydroxy-substituted benzils are listed in Table IV as a function of "pH". The data for the corresponding hydroxy-substituted benzaldehydes are listed in Table V. The spectra for "pH's" 1.5, 3, and 5 were identical and only the "pH" 1.5 data are reported. The spectrum of p-anisil was not influenced by "pH". The second maximum of p-anisoin at "pH" 13.5 was shifted to a longer wavelength which was almost identical to the second maximum of p-anisil. This indicates that the p-anisoin is air oxidized to p-anisil at the high "pH". The p-anisoin spectrum was not influenced at lower "pH's".

The spectrum of 3,3',4,4'-tetrahydroxybenzil at "pH" 13.5 is distinctly different from the spectrum at "pH" 11.3. The two maxima at 332 and 390 mμ in "pH" 13.5 buffer could be caused by the ionization of the meta-hydroxyl groups or by some rearrangement.

The ultraviolet spectra of the benzaldehyde derivatives were obtained in order to compare their molar absorptivities with the molar absorptivities of the corresponding benzil derivatives. The molar absorptivity ratio of equal molar solutions of benzil derivatives to benzaldehyde derivatives was approximately 1.75 in acidic solutions and 1.40 in basic solutions.

TABLE IV

ULTRAVIOLET SPECTRA OF BENZIL DERIVATIVES

Compound	"pH"	λ_{max}, mμ	ϵ_{max}	λ_{max}	ϵ_{max}	λ_{max}	ϵ_{max}
3,3',4,4'-	1.5	233.0	22,160	288.0	18,760	332.0	18,690
Tetrahydroxy-	7.2	--[a]	--	286.0	18,090	335.0	17,730
benzil						368.0	11,700
	9.0	252.5	13,470	--	--	373.0	34,010
2.82×10^{-5} M	11.3	253.0	14,820	--	--	374.0	38,290
	13.5	263.0	13,120	332.0	11,170	390.0	22,730
p,p'-Dihydroxy-	1.5	223.5	16,380	302.0	27,190	--	--
benzil	7.2	--[a]	--	301.0	24,500	359.0	3,930
	9.0	245.0	7,920	300.0[b]	12,690	359.0	35,110
3.31×10^{-5} M	11.3	245.0	9,550	299.0[b]	9,850	361.0	41,690
	13.5	245.0	9,670	--	--	360.5	45,860
Vanillil	1.5	231.5	21,700	290.0	16,570	331.0	19,590
	7.2	--[a]	--	289.0	14,080	332.0	17,360
2.65×10^{-5} M						370.0	9,510
	9.0	253.5	12,830	290.0[b]	7,890	375.0	34,720
	11.3	254.0	15,660	--	--	377.0	40,940
	13.5	250.0	12,980	--	--	378.0	39,930
Syringil	1.5	230.0	29,860	337.0	22,080	--	--
	7.2	--[a]	--	337.0	18,510	390.0	11,580
2.21×10^{-5} M	9.0	250.0	15,660	--	--	395.0	34,840
	11.3	251.0	17,380	--	--	398.0	39,010
	13.5	251.0	16,740	--	--	398.0	38,780
m,m'-Dihydroxy-	1.5	--[a]	--	266.0	18,910	326.0	5,170
benzil	7.2	--[a]	--	266.0	18,700	326.0	4,890
	9.0	--	--	265.0	38,610	326.0	10,030
3.31×10^{-5} M	11.3	245.5	35,050	280.0	15,590	378.0	4,290
	13.5	245.5	35,650	280.0	14,800	378.0	4,290
p-Anisil	all "pH's"	221.0	16,050	301.0	29,630	--	--
2.96×10^{-5} M							
p-Anisoin	1.5	222.0	17,680	282.5	15,470	--	--
	13.5	222.0	16,490	300.0	27,890	--	--
2.94×10^{-5} M							

[a] The solvent-buffer system absorbed before the organic compound.

[b] A shoulder on the rise of the maximum at the longer wavelength.

TABLE V

ULTRAVIOLET SPECTRA OF BENZALDEHYDE DERIVATIVES

Compound	"pH"	λ_{max}, mμ	ϵ_{max}	λ_{max}	ϵ_{max}	λ_{max}	ϵ_{max}
3,4-Dihydroxy-	1.5	232.5	13,450	281.5	10,380	314.0	9,030
benzaldehyde	7.2	--[a]	--	281.5	9,410	315.0[b]	8,550
						348.0[b]	2,590
	9.0	250.0	7,760	290.0[b]	3,830	348.0	20,310
2.82×10^{-5} M	11.3	250.0	8,720	--	--	349.0	23,860
	13.5	261.5	6,200	320.0	9,550	360.0	11,720
						394.0	10,510
p-Hydroxy-	1.5	223.5	11,660	285.5	16,980	--	--
benzaldehyde	7.2	--[a]	--	285.5	16,490	333.0	1,380
	9.0	225.0	5,790	294.0	7,680	335.5	21,950
3.30×10^{-5} M		241.0	5,610				
	11.3	241.0	7,770	295.9[b]	5,030	335.0	31,400
	13.5	240.5	8,080	295.9[b]	5,030	335.0	32,170
Vanillin	1.5	231.5	14,720	281.0	10,340	311.0	10,380
	7.2	--[a]	--	281.0[b]	9,620	312.0	9,430
2.63×10^{-5} M	9.0	235.0	6,880	285.0[b]	4,250	351.0	22,360
		251.5	7,870				
	11.3	251.0	8,900	295.0[b]	2,440	352.0	28,140
	13.5	251.5	8,740	295.0[b]	2,350	352.0	28,440
Syringalde-	1.5	230.5	15,770	309.0	13,410	--	--
hyde	7.2	--[a]	--	310.0	12,730	--	--
	9.0	253.0	11,860	365.0	21,050	--	--
2.20×10^{-5} M	11.3	253.5	14,400	368.0	26,730	--	--
	13.5	253.0	13,500	367.5	26,360	--	--

[a] The solvent buffer system absorbed before the organic compound.

[b] A shoulder on the maximum at the longer wavelength.

POLAROGRAPHIC RESULTS AND DISCUSSION

At least one polarographic wave was produced for each of the compounds studied at all "pH's". There was also a second more negative wave at higher "pH's". The second waves were helpful in determining the reduction products of the first waves, but the primary emphasis in this study has been the investigation of the first waves.

The first waves for all compounds were two-electron reductions. These waves were more irreversible in the acid than in the basic solutions. The waves were not completely diffusion controlled. The half-wave potentials were "pH" dependent over the "pH" range 1.5 to 13.5. The "pH" dependence was different in the acid and basic solutions. Electron-releasing substituents made the reductions harder (more negative half-wave potentials). Solvent-solute interactions, such as hydrogen bonding and ionization, were evident for the hydroxy-substituted compounds. These solvent effects complicated the reductions of the hydroxy-substituted compounds to such an extent that no quantitative correlation of structure and reactivity was obtained. A kinetic analysis of the data showed there was more than one irreversible process for the reductions.

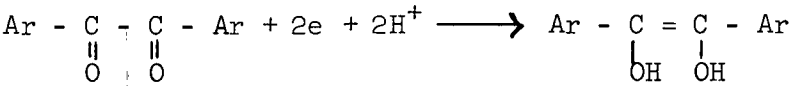
Elving (55) states, "the half-wave potential for an irreversible polarographic wave can seldom be reproduced to less than $\pm$ 10 millivolt." The experimental errors in measuring the half-wave potentials in this investigation were equal to or less than $\pm$ 10 mv., except for 3,3',4,4'-tetrahydroxybenzil. The irreversibility of this compound was greater than the other compounds.

The half-wave potentials are given to three decimal places throughout this thesis for comparative purposes only.

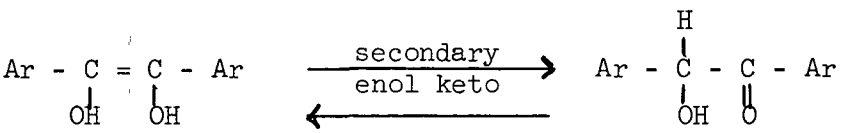
DESCRIPTION OF THE POLAROGRAPHIC WAVES

One polarographic reduction wave was produced at "pH's" 1.5 to 7.2, and two waves were produced at "pH's" 9, 11.3, and 13.5 for all compounds except 3,3',4,4'-tetrahydroxybenzil which produced no second wave at "pH" 13.5. The limiting currents of the second waves increased with increasing "pH". The limiting currents of the first waves were similar for all compounds.

It has been shown (13, 23) that benzil is reduced to the enediol of benzoin, which then rearranges to the keto form. The enediol is not reducible at the DME. The enol to keto rearrangement is facilitated in alkaline solution so that the enediol rearranges to the reducible keto form before it diffuses away from the electrode. A second wave for the reduction of benzoin is then produced.



Benzil — Enediol Form



Benzoin

An ideal method to determine the polarographic reduction product of a particular compound is to reduce the expected reduction product at the same conditions. If the second wave of the particular compound has the same $E_{1/2}$ as the first wave of the expected reduction product, it can be concluded that the reduction product is the expected one.

p-Anisoin and vanilloin were reduced at all "pH's" since these are the reduction products of p-anisil and vanillil as indicated from controlled potential electrolyses (p. 28 to 31). Benzoin also was reduced for comparison purposes since it is the reduction product of benzil.

Provided that p-anisil and vanillil are reduced to their enediols, as reported for benzil, a second wave for these compounds would not be expected unless the enediols rearranged to the keto forms before they diffused away from the electrode. p-Anisoin, vanilloin, and benzoin should produce reduction waves at all "pH's". The $E_{1/2}$'s of these waves should be similar to the $E_{1/2}$'s of the second waves of p-anisil, vanillil, and benzil at "pH's" 9, 11.3, and 13.5.

The data presented in Table VI show that benzoin, p-anisoin, and vanilloin produce reduction waves at all "pH's". The fact that p-anisil and vanillil do not have a second wave at "pH's" 1.5 to 7.2, and that p-anisoin and vanilloin were identified as the controlled potential reduction products at these "pH's", indicates that the enediols are the electrode reduction products. This statement is supported by the fact that benzil behaves accordingly.

TABLE VI

HALF-WAVE POTENTIALS FOR BENZOIN, p-ANISOIN, VANILLOIN, AND FOR THE SECOND WAVE OF BENZIL, p-ANISIL, AND VANILLIL

	$-E_{1/2}$, volts						
"pH"	1.5	3.0	5.0	7.2	9.0	11.3	13.5
Benzoin	0.860	0.966	1.156	1.291	1.354	1.504	1.530
p-Anisoin	0.874	--	1.215	1.389	1.430	1.581	1.627
Vanilloin	0.987	1.125	1.320	--[a]	1.503	1.763	1.818
Benzil[b]	--	--	--	--	1.393	1.516	1.545
p-Anisil[b]	--	--	--	--	1.450	1.596	1.624
Vanillil[b]	--	--	--	--	1.464	1.758	1.802

[a]Solvent-supporting electrolyte system decomposed before the reduction occurred.

[b]No second wave was produced for benzil, p-anisil, and vanillil at "pH's" 1.5 to 7.2.

The $E_{1/2}$'s of the second waves of p-anisil and vanillil are identical with the $E_{1/2}$'s of p-anisoin and vanilloin (within experimental error) at "pH's" 11.3 and 13.5. At "pH" 9 the $E_{1/2}$ values are not identical within experimental error. However, at this "pH" the currents produced for the second waves of the benzils were 1/10 the currents produced for the benzoins. This introduces an additional error into the calculation of the $E_{1/2}$'s. Again the benzil and benzoin reductions at "pH's" 9, 11.3, and 13.5 are similar to those just discussed for p-anisil, p-anisoin, vanillil, and vanilloin.

The data just presented and the fact that the reduction of p-anisil and vanillil requires two electrons, as determined from controlled potential electrolyses, indicates that the reduction of p-anisil and vanillil is the same as that reported for benzil (13, 23).

The limiting currents for all benzil derivatives were similar. The limiting current is dependent upon the number of electrons involved in the reduction as seen from the Ilkovic Equation (6). Since the other terms of this equation were held constant, it follows that the number of electrons involved in the reductions of the other benzil derivatives equals two, as shown for benzil, p-anisil, and vanillil. It was stated earlier (p. 40) that the number of waves produced at a given "pH" was the same for all the benzil derivatives. Therefore, it can be assumed that the reduction products of the benzil derivatives are their respective enediols as was shown for benzil, p-anisil, and vanillil. However, the rates of the secondary rearrangements to the keto forms are probably influenced by the substituents.

The polarograms of benzoin, p-anisoin, and vanilloin were recorded by the procedure described on page 27. At "pH" 13.5 these compounds produced two waves but at lower "pH's" only one wave was produced. The first waves at "pH" 13.5

had the same $E_{1/2}$'s as the corresponding benzils. If the "pH" 13.5 buffer solution was deaerated before adding the benzoins, only one wave was produced. If the nitrogen was stopped for 15 minutes and then another polarogram recorded, two waves were produced. Chodkowska and Grabowski (13) also reported this phenomenon for benzoin, and state that benzil is easily formed in alkaline media by accidental oxidation of benzoin. Keto to enol rearrangements are known to be base catalyzed (51). Therefore, it appears that the enediol to benzoin rearrangement is rapid for benzoin, p-anisoin, and vanilloin at "pH" 13.5. The ultraviolet spectrum of p-anisoin in "pH" 13.5 buffer solution also indicates that p-anisoin is oxidized to p-anisil. See page 37.

NATURE OF THE ELECTRODE PROCESS

REVERSIBILITY OF THE ELECTRODE PROCESS

The potential of a thermodynamic reversible electrode reaction is the equilibrium potential acquired by an electrolytic solution when there is no current flowing through the system. When an attempt is made to carry out a reaction at an appreciable rate, the potential of the electrode must be changed from the equilibrium potential in such a direction as will sustain the flow of current. The greater the current or resistance to current flow the greater is the change of potential, and the greater is the irreversibility of the electrode process.

Overpotential is a measure of the degree of irreversibility of an electrode reaction. Overpotential is the difference between the equilibrium potential and the potential required to sustain a current flow. Therefore, the greater the overpotential the more irreversible the electrode process.

Reversible electrode processes occur at finite rates, and hence, cannot be considered strictly as thermodynamically reversible reactions. However, Lingane

has stated, "there are many cases where the potential of a working electrode is so slightly greater than the reversible potential computed from the concentration at the electrode surface, that the difference between the two approaches experimental error" (56).

The transfer coefficient (α) is used to designate the fraction of the applied electrode potential which favors the electrode reaction in the forward direction, and ($1-\alpha$) is the fraction of the applied electrode potential which hinders the backward reaction. The value of α equals unity for a reversible electrode reaction. The irreversibilities of electrode reactions are often referred to as more or less irreversible depending upon the deviation of α from unity.

One criterion of reversibility of an electrode reaction is that a plot of log $[i/(i_D - i)]$ vs. E from Equation (7) produces a straight line and that the slope of this line is equal to $0.0591/\alpha n$. Any deviation of the slope greater than 3 to 5 millivolts is, according to Meites (57), "fairly conclusive proof of some degree of irreversibility."

The potential of an irreversible wave at any point is determined not only by the rate of diffusion of the reducible and reduced species to and from the electrode, but also by the rates of the various processes (both chemical and electrochemical) occurring at the drop-solution interface. The meaning of the slope of a plot of Equation (7) for an irreversible electrode process is not clearly understood. The slope of an irreversible electrode process is determined by the relative magnitude of the charge of the reducible species (z), the number of electrons transferred (n_a), the potential difference between the interior of the electrode and the reaction site (ϕ), and the change of (ϕ) with potential (58). Keeping this in mind, the slope determined from a plot of

Equation (7) is not a direct measure of the degree of irreversibility, but only an indication of it.

In order to apply this test for reversibility [plot of Equation (7)] of an electrode reaction it is necessary to have an independent estimate of the number of electrons involved in the electrode reduction. It has been determined by controlled potential electrolyses and the polarographic reductions of benzoins, that two electrons are involved in the electrode reactions of this investigation.

The values of αn were calculated from the slopes of the least squares correlations obtained from the computer program mentioned on page 15. For a reversible electrode process the value of αn equals two. Any deviation of αn greater than $\pm$ 0.15 (1.85 to 2.15) is an indication of the degree of irreversibility of the electrode reactions.

The αn values are presented in Table VII.

TABLE VII

THE EFFECT OF HYDROGEN ION CONCENTRATION ON αn

"pH"	Benzil	m-Anisil	p-Anisil	m,m'-Dihydroxybenzil	Syringil	Vanillil	p,p'-Dihydroxybenzil	Tetrahydroxybenzil
1.5	1.02	1.01	1.04	1.15	1.00	0.85	0.77	0.57
3.0	0.88	1.01	0.91	0.70	0.90	0.71	0.48	0.22
5.0	1.05	1.61	1.09	0.82	1.05	0.71	0.57	0.51
7.2	1.23	1.43	1.26	1.01	0.78	0.96	0.93	0.99
9.0	1.76	2.09	1.81	1.59	1.21	1.12	1.05	0.92
11.3	2.05	2.09	1.60	1.71	0.95	0.99	0.81	0.87
13.5	2.06	2.10	2.10	1.15	1.31	1.05	1.09	0.47

The points of interest of these data are the following:

(1) The αn values have a minimum at "pH" 3.

(2) The αn values increase with increasing "pH" indicating a more reversible process at the higher "pH's". The reductions at "pH's" 9.0, 11.3, and 13.5 for m-anisil, at "pH's" 11.3 and 13.5 for benzil, and at "pH" 13.5 for p-anisil are reversible.

(3) The αn values of m,m'-dihydroxy- and tetrahydroxybenzil are less at "pH" 13.5 than at "pH's" 9 and 11.3.

(4) The αn values of the nonhydroxy-substituted compounds are greater than those for the hydroxy-substituted compounds with the exception of syringil in the acid region and m,m'-dihydroxybenzil at "pH" 1.5. In general, the greater the electron-releasing ability of the substituents, the less the αn value.

(5) Excluding 3,3',4,4'-tetrahydroxybenzil, the αn values for all compounds are more nearly uniform at "pH" 1.5.

Many investigators have shown that the nature of the anions and cations of the supporting-electrolyte affect the reductions of irreversible inorganic systems (58-61). Reinmuth, Rogers, and Hummelstedt (58) have indicated that the anion of the supporting electrolyte affects αn on the anodic side of the electrocapillary maximum, (ECM)*, and that the cation affects αn on the cathodic side. A minimum is observed for αn in the vicinity of the ECM. Lothe and Rogers (62) working with carbon tetrachloride and Rosenthal, Albright, and Elving (63) working with C_3 to C_8 α-bromo-n-alkanoic acids found this parabolic shape of αn with $E_{1/2}$ as the pH was changed.

*The ECM is the potential when the net charge of a thin layer of solution immediately surrounding the drop is zero. At this point there is no preferential adsorption of ions.

The ECM can be associated with the maximum of a plot of drop time vs. $\underline{E}$ (64). The ECM is between -0.23 and 0.40 volt as shown on Fig. 3. The $\underline{E}_{1/2}$'s at "pH" 3.0 are close to the ECM for the compounds studied. Therefore, the minimum $\alpha\underline{n}$ values at "pH" 3.0 are probably due to the ECM.

Figure 6 illustrates the typical logarithmic plots obtained for the compounds with various $\alpha\underline{n}$ values. The smaller the $\alpha\underline{n}$ value, the more the plots deviate from straight lines. Meites (65) states that straight-line log plots can be secured for irreversible waves. "Often, however, the plots are not straight but curved, and sometimes may even be found to consist of two intersecting straight lines." This type of plot is good evidence of an irreversible wave.

Another criterion of polarographic reversibility is that the $\underline{E}_{1/2}$ be constant and independent of the concentration of reducible species. The $\underline{E}_{1/2}$'s for irreversible waves often vary with concentration, and they usually become more negative as the concentration increases. The effect of concentration on $\underline{E}_{1/2}$ is shown in Table VIII.

The insignificant variation of the $\underline{E}_{1/2}$ of benzil with concentration indicates that it is reversibly reduced in unbuffered solutions. The "pH" at the DME in the unbuffered solution is approximately 11.1 as estimated by comparing the $\underline{E}_{1/2}$ in unbuffered solution with the $\underline{E}_{1/2}$'s of buffered solutions in Fig. 9. The $\alpha\underline{n}$ values of benzil at the higher "pH's" (11.3 and 13.5) also indicated a reversible reaction. Therefore, the two tests of reversibility ($\alpha\underline{n}$ values and the variation of $\underline{E}_{1/2}$ with concentration) are in agreement.

The variations of the $\underline{E}_{1/2}$'s of $\underline{p}$-anisil and vanillil with concentration are greater than experimental error in the "pH" 7.2 buffered solution. Therefore, these two compounds are irreversibly reduced at "pH" 7.2. Again the two

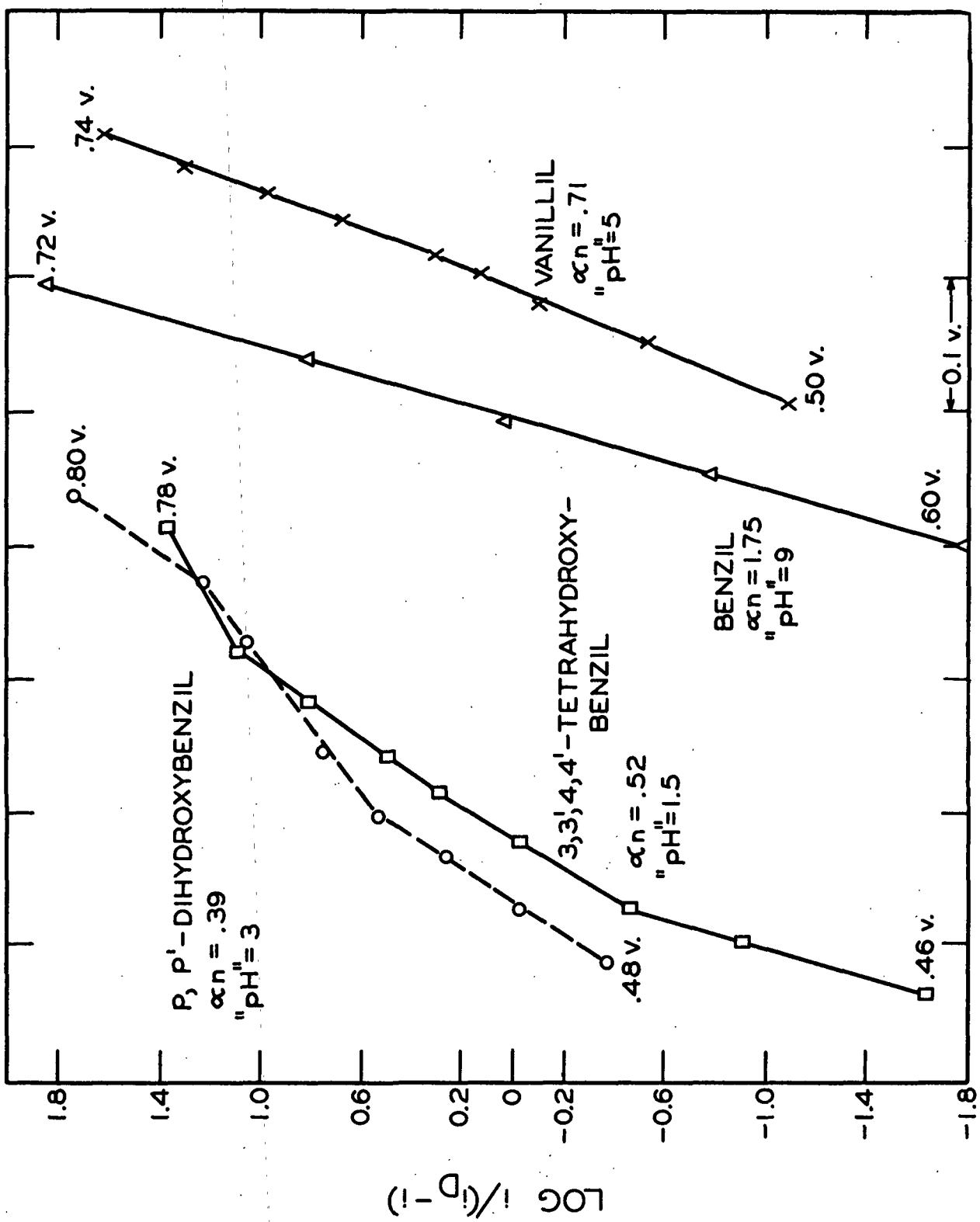


Figure 6. Typical Log $i/(i_D - i)$ vs. E Plots

tests of reversibility are in agreement, since the αn values of p-anisil and vanillil (Table VII) also indicated an irreversible reduction.

TABLE VIII

EFFECT OF CONCENTRATION ON BENZIL, p-ANISIL, AND VANILLIL AT 25°C.

Concn., mmole/l.	i_D/C $\left(\frac{\mu a. - l.}{mmole}\right)$	$-E_{1/2}$ vs. s.c.e., volts
Benzil in Unbuffered Solution, 0.15M LiCl		
0.5	4.00	0.751
1.0	4.23	0.753
1.5	4.25	0.755
2.0	4.17	0.767
p-Anisil at "pH" 7.2		
0.5	3.98	0.681
1.0	4.48	0.700
2.0	3.06	0.688
Vanillil at "pH" 7.2		
0.1	3.79	0.813
0.5	3.33	0.793
1.0	3.58	0.778

CURRENT CONTROLLING ELECTRODE PROCESS

An electrode process is controlled by diffusion if i_D/C is independent of concentration. Any variation of i_D/C with concentration is evidence that the limiting current is not totally diffusion controlled, but is partially governed by the actual rate of the electrode process. The values of i_D/C for benzil, p-anisil, and vanillil are given in Table VIII.

The small variation of i_D/C with concentration for benzil indicates that the reduction is diffusion controlled in the unbuffered solution. The variations of i_D/C with concentration for p-anisil and vanillil indicate that the currents are partially controlled by the rate of the electrode process at the "pH" (7.2) studied.

Another test to determine if the current is diffusion controlled is the effect of the temperature on the limiting current. The temperature coefficient of i_D, found by differentiating the Ilkovic Equation (6) with respect to temperature, is practically equal to one-half of the temperature coefficient of the diffusion coefficient of the reducible species.

The temperature coefficient of i_D of organic compounds should not be much larger than +2 to 3% per degree for a diffusion-controlled process. Much higher values than this are found if the current is rate-controlled. This is further assured if the temperature coefficient itself is found to change markedly with temperature (66).

In Table IX are given the i_D's and the $E_{1/2}$'s for benzil, p-anisil, and p,p'-dihydroxybenzil in several buffer solutions at temperatures 25.00, 30.10, and 40.10°C. The values of i_D were used to calculate the temperature coefficients of the limiting currents according to the following equation (66):

$$\frac{\Delta i_D}{\Delta T} = (i_{D2}/i_{D1})^{1/(T_2 - T_1)} - 1$$

where i_{D2} and i_{D1} are the limiting currents measured at temperature T_2 and T_1, respectively.

The temperature coefficients from 25 to 40.1°C. (last column of Table IX) for the i_D's of benzil and p-anisil compare favorably with the predicted temperature coefficient for a diffusion-controlled process. The variation of the temperature coefficients with temperature from 25 to 30.1°C. and 30.1 to 40.1°C. may indicate that the i_D's are slightly dependent on some rate-controlling process.

The temperature coefficients from 25 to 30.1°C. and 30.1 to 40.1°C. for the i_D's of p,p'-dihydroxybenzil are conclusive proof that the current is rate-controlled

TABLE IX

TEMPERATURE DEPENDENCE OF i_D AND $E_{1/2}$ OF BENZIL, p-ANISIL, AND p,p'-DIHYDROXYBENZIL, 0.5×10^{-3} M, IN SEVERAL BUFFER SOLUTIONS

pH	Temp., °C.	$-E_{1/2}$ vs. s.c.e., volts	i_D, μa.	Temp. Coeff. of i_D, %
Benzil				
1.5	25.0	0.259	2.325	1.21 } 1.86
	30.1	0.255	2.447	2.26 }
	40.1	0.260	3.072	
3.0	25.0	0.354	2.496	1.44 } 1.23
	30.1	0.363	2.694	1.06 }
	40.1	0.366	3.008	
9.0	25.0	0.670	2.274	1.38 } 2.06
	30.1	0.666	2.436	2.35 }
	40.1	0.664	3.081	
13.5	25.0	0.824	2.015	3.67 } 2.31
	30.1	0.836	2.423	1.76 }
	40.1	0.842	2.885	
p-Anisil				
1.5	25.0	0.339	1.928	3.76 } 2.40
	30.1	0.325	2.279	1.89 }
	40.1	0.327	2.784	
9.0	25.0	0.729	1.903	3.82 } 2.38
	30.1	0.736	2.301	1.65 }
	40.1	0.724	2.717	
13.5	25.0	0.903	2.018	1.75 } 1.89
	30.1	0.913	2.210	1.95 }
	40.1	0.914	2.678	
p,p'-Dihydroxybenzil				
1.5	25.0	0.352	1.843	12.50 } 1.78
	30.1	0.363	3.354	-3.35 }
	40.1	0.344	2.413	
3.0	25.0	0.511	1.764	13.62 } 2.06
	30.1	0.526	3.370	-3.43 }
	40.1	0.520	2.402	
9.0	25.0	0.974	1.681	13.05 } 2.06
	30.1	0.981	3.130	-3.18 }
	40.1	0.932	2.287	
13.5	25.0	1.383	1.663	13.09 } 2.02
	30.1	1.394	3.099	-3.25 }
	40.1	1.381	2.253	

at the "pH's" investigated. However, the temperature coefficients of the i_D's from 25 to 40.1°C. indicate a diffusion-controlled process. These conflicting data indicate that the effect of temperature on the electrode reduction of p,p'-dihydroxybenzil is complicated. There could be a change in mechanism at 30°C. which would require more or less than two electrons for the reduction. A solvent-solute interaction also could be responsible for the conflicting temperature coefficients. These two possibilities will now be examined.

If the electrode reaction of p,p'-dihydroxybenzil at 30°C. is due to a change in the number of electrons and, therefore, a change in mechanism, the αn value at 30.1°C. should be different. The αn values for p,p'-dihydroxybenzil, benzil, and p-anisil were calculated at 30.1 and 40.1°C. and compared with the values at 25.0°C. There was a small variation with temperature, but the αn values for benzil and p-anisil varied as much as the αn values for p,p'-dihydroxybenzil. Therefore, it does not appear that there is a change in the number of electrons involved in the reductions at 30.1°C.

The deviation of the αn values of p,p'-dihydroxybenzil from two in Table VII indicates that it is irreversibly reduced at the DME. Kolthoff and Lingane (67) state that the variation of $E_{1/2}$ with temperature is related to the activation energy of the irreversible step in the electrode reaction. The $E_{1/2}$'s of p,p'-dihydroxybenzil in Table IX are more negative at 30°C., but the variation is not much greater and sometimes less than experimental error. This small change in the $E_{1/2}$ at 30°C. could indicate that an irreversible step is responsible for the conflicting temperature coefficient values of i_D's.

The hydroxyl groups of p,p'-dihydroxybenzil can be affected by solvent-solute interactions such as ionization and hydrogen bonding. These interactions would not greatly affect benzil and p-anisil and also could be irreversible steps in

the electrode reduction of p,p'-dihydroxybenzil. Delahay and Mattax (61) state that occurrence of temperature-dependent stepwise processes complicate the effect of temperature on an electrode reaction.

The potentiometric titrations indicate that ionization does not occur until "pH" 5. Since the temperature effect occurs at "pH's" 1.5 and 3.0, the ionization of the hydroxyl groups does not appear to be responsible. However, there is a possibility that the hydroxyl groups could be ionized at the electrode, due to the high electric field.

Hydrogen bonding appears to be a better explanation since it has been reported that spectacular reductions in the infrared intensities of hydroxyl association bands may accompany a temperature rise of 10 to 20°C. (68). Finch and Lippencott (69) studied methanol, ethanol, o-chlorophenol, and phenol in ether over the temperature range -93 to 65°C. They concluded that temperature affects both the infrared frequency and the absorption of each particular hydrogen-bonded species. Liddel and Becker (70) report a 36% decrease in intensity and a 0.2% increase in frequency for monomeric methanol (0.005M) in carbon tetrachloride. Others (71-73) have reported the same absorbance behavior for dilute solutions of phenols in hexachlorobutadiene. Coggeshall and Saier (74) have showed that association may occur between hydroxylated material, such as ethanol (0.015M), and proton acceptor materials such as acetone and dioxane (0.235M) in carbon tetrachloride. Hughes, Martin, and Coggeshall (71) explain that the infrared intensity decrease is due to a decrease in intensity of the force field on a molecule due to its neighbors, since the average distance between molecules becomes greater as the temperature increases.

The above studies were for solute-solute or intermolecular hydrogen bonding. The concentration employed in this study (0.0005M) is too dilute for intermolecular

hydrogen bonding between two dihydroxybenzil molecules (75). However, there are possibilities for solvent-solute hydrogen bonding as will be shown later with diffusion coefficient calculations, page 60. The temperature increase could decrease the amount of solvent-solute hydrogen bonding. This would increase the diffusion coefficient of p,p'-dihydroxybenzil and, therefore, the limiting current would increase, as shown by the Ilkovic Equation (6).

It now appears that the temperature coefficients of the i_D's of p,p'-dihydroxybenzil are due to solvent-solute interactions, especially hydrogen bonding, rather than a change in the number of electrons involved in the reduction process.

KINETICS OF THE ELECTRODE PROCESS

The previous data have shown that the majority of the polarographic waves are irreversible. A kinetic analysis of the data was done to determine the rate constants of the electrode reactions. The Koutecky procedure (31) for totally irreversible waves controlled by one rate-determining process was used for the analysis. The calculations were made for all waves using a computer program (IBM 1620) previously mentioned on page 17.

The test for one rate-determining process in an irreversible electrochemical reduction is that a plot of log $k_{f,h}$ vs. E yields a straight line. Except for benzil, m-anisil, and p-anisil at "pH" 13.5, and benzil and m-anisil at "pH" 11.3, plots of log $k_{f,h}$ vs. E from Equation (13) did not produce straight lines, but showed inflections. This indicates that the electrode reactions are more complicated than the single-rate-determining process assumed by Koutecky in deriving Equation (11) for irreversible polarographic waves. Figures 7 and 8 are typical plots of log $k_{f,h}$ vs. E for data at "pH's" 1.5 and 13.5.

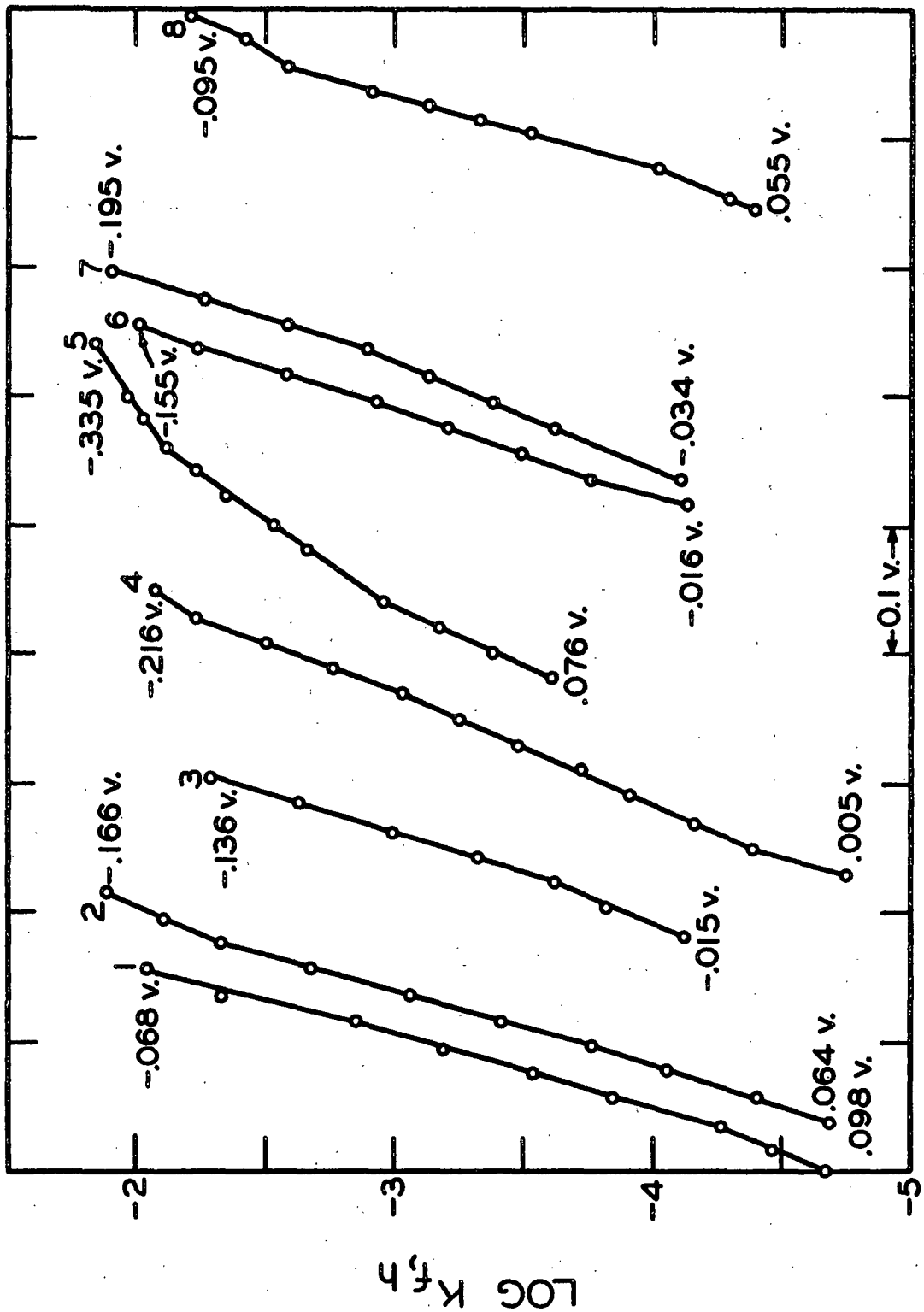


Figure 7. Log $k_{f,h}$ vs. E at "pH" 1.5. The $k_{f,h}$ values were calculated by the Koutecky method.
1. m-Anisil; 2. Benzil; 3. p-Anisil; 4. p,p'-Dihydroxybenzil; 5. 3,3',4,4'-Tetrahydroxybenzil; 6. Syringil; 7. Vanillil; 8. m,m'-Dihydroxybenzil

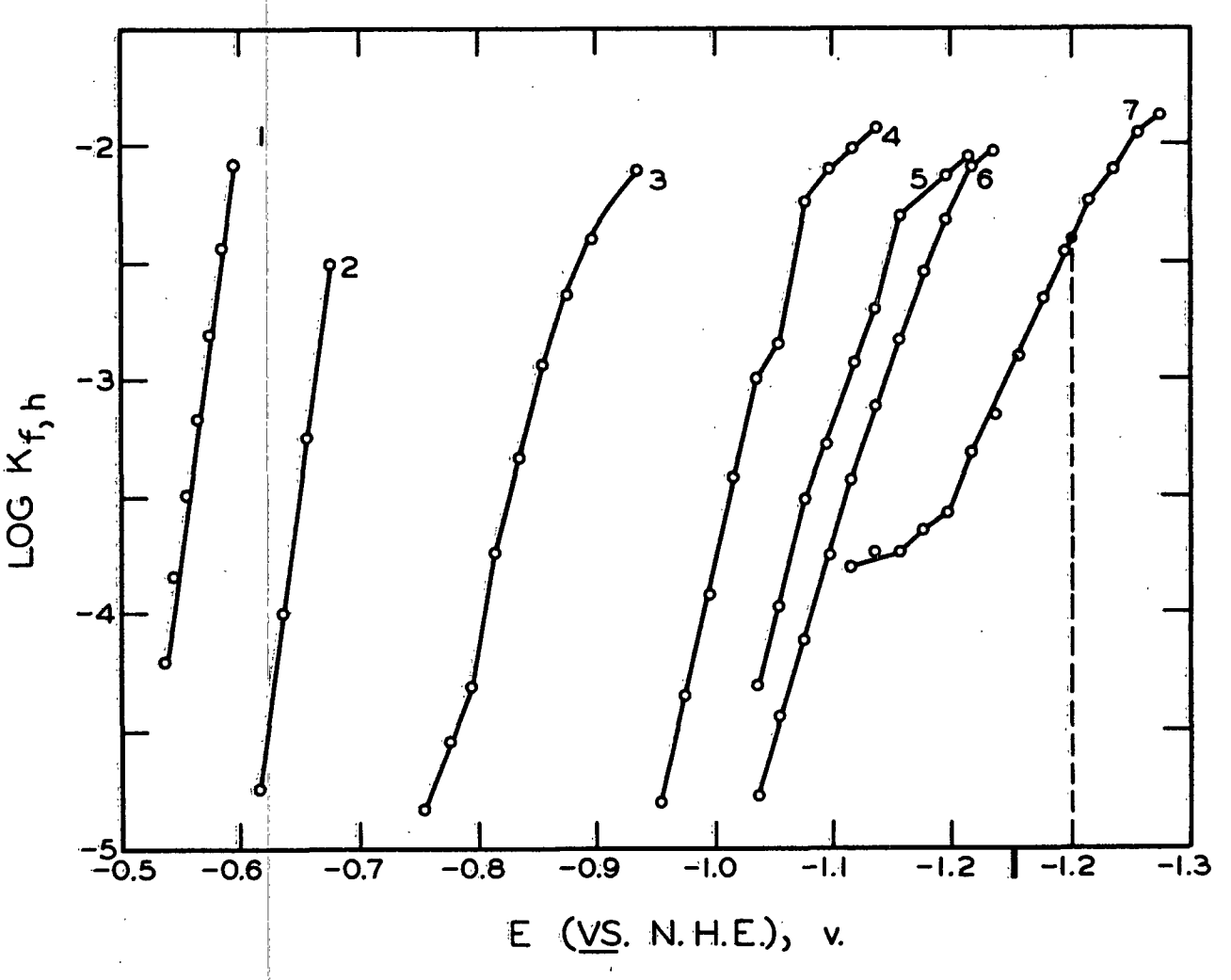


Figure 8. Log $k_{f,h}$ vs. E at "pH" 13.5. The $k_{f,h}$ values were calculated by the Koutecky method. 1. Benzil and m-Anisil; 2. p-Anisil; 3. m,m'-Dihydroxybenzil; 4. Syringil; 5. Vanillil; 6. p,p'-Dihydroxybenzil; 7. Tetrahydroxybenzil

The linear log $k_{f,h}$ vs. E relationships of benzil, m-anisil, and p-anisil are not understood since these compounds are reversibly reduced at "pH" 13.5, and an analysis for irreversible waves was used to obtain the relationships.

Some of the log $k_{f,h}$ vs. E plots exhibited more than one inflection point. The significance of this has not been ascertained to date. Therefore, it can only be concluded that there is more than one irreversible step for these electrode reactions.

The physical significance of the rate constant $k^{o}_{f,h}$ obtained from the intercept at zero potential versus a NHE is uncertain. The values of $k^{o}_{f,h}$ were used to calculate the $E_{1/2}$'s of the irreversible waves from Equation (10). These $E_{1/2}$'s agreed within 5 mv. with the $E_{1/2}$'s obtained by using Equation (7) for reversible waves. The log $k^{o}_{f,h}$ values are given in Table X. Some qualitative idea of the variation of the kinetics of the electrode reactions may be apparent from the values.

TABLE X

VARIATION OF LOG $k^{o}_{f,h}$, CM./SEC. WITH "pH"

"pH"	1.5	3.0	5.0	7.2	9.0	11.3	13.5
Benzil	-3.41	-4.72	-6.92	-9.00	-13.66	-20.42	-23.37
m-Anisil	-3.09	-5.75	-7.66	-10.31	-15.63	-18.48	-21.44
p-Anisil	-4.78	-4.85	-7.07	-9.36	-14.74	-19.37	-21.31
m,m'-Dihydroxy-benzil	-2.90	-4.75	-6.47	-9.05	-12.36	-20.05	-15.72
Syringil	-4.44	-5.46	-7.83	-8.78	-13.69	-17.61	-20.43
Vanillil	-4.37	-5.58	-7.12	-11.57	-14.42	-20.49	-18.84
p,p'-Dihydroxy-benzil	-4.74	-5.05	-7.46	-11.31	-13.04	-15.39	-20.10
Tetrahydroxy-benzil	-4.55	-4.73	-7.29	-13.32	-13.62	-17.32	-9.49

The nature of the electrode processes can be summarized as follows:

(1) The reversibility of the process increases with increasing "pH". This is due to the role of the hydrogen ion in the electrode reduction and also to the affect of "pH" on the keto-enol equilibrium of the reduction product.

(2) The hydroxy-substituted compounds are more irreversible than the nonhydroxy-substituted compounds. This is due to solvent interactions, such as ionization and hydrogen-bonding.

(3) The current is partially controlled by the rate of reaction and diffusion for all compounds at all "pH's" with the exception of benzil, p-anisil, and possibly m-anisil at a "pH" greater than 11.

(4) There is more than one irreversible process for the reductions of all compounds at all "pH's" except benzil, m-anisil, and p-anisil at "pH" 13.5.

EFFECT OF HYDROGEN ION CONCENTRATION ON THE POLAROGRAPHIC WAVES

The $E_{1/2}$ and i_D values for the compounds polarographically reduced are shown in Table XI. The values shown are averages of four polarograms and were obtained with the computer program which solved the Heyrovsky-Ilkovic Equation (7).

EFFECT ON THE LIMITING CURRENT

The limiting current values for each compound were corrected for the variation of the product $m^{2/3}\ t^{1/6}$ with potential. This variation is shown in Fig. 3. The potential of the limiting current at "pH" 1.5 was selected as the base and the i_D's at the other "pH's" were corrected to this potential.

TABLE XI

THE EFFECT OF HYDROGEN ION CONCENTRATION ON $E_{1/2}$ AND i_D, AT 25°C.

	"pH"	Benzil	m-Anisil	p-Anisil	m,m'-Dihydroxybenzil	Syringil	Vanillil	p,p'-Dihydroxybenzil	Tetrahydroxybenzil
1.5	$-E_{1/2}$, v.	0.259	0.232	0.339	0.246	0.313	0.331	0.352	0.397
	i_D, μa.	2.325	2.037	1.928	1.866	1.740	1.851	1.843	2.596[a]
3.0	$-E_{1/2}$	0.354	0.345	0.434	0.363	0.407	0.456	0.511	0.683
	i_D	2.499	2.078	2.007	1.820	1.721	1.780	1.772	2.837
5.0	$-E_{1/2}$	0.477	0.448	0.549	0.499	0.555	0.616	0.737	0.812
	i_D	2.205	1.998	1.987	1.874	1.708	1.721	1.786	2.618
7.2	$-E_{1/2}$	0.614	0.580	0.668	0.647	0.707	0.793	0.839	0.885
	i_D	2.190	1.951	2.000	1.875	1.721	1.677	1.798	2.698
9.0	$-E_{1/2}$	0.670	0.640	0.729	0.698	0.863	0.936	0.974	1.058
	i_D	2.286	1.989	1.916	1.817	1.574	1.644	1.703	2.590
11.3	$-E_{1/2}$	0.802	0.764	0.889	0.958	1.268	1.342	1.369	1.398
	i_D	2.147	1.987	1.885	1.604	1.621	1.600	1.718	2.546
13.5	$-E_{1/2}$	0.824	0.811	0.903	1.075	1.269	1.346	1.383	1.334
	i_D	2.030	1.921	2.037	1.664	1.753	1.790	1.712	2.605

[a]The concentration of reducible species was 0.0052M for this compound. It was 0.0005M for all the other compounds.

The experimental error for the limiting current was $\pm$ 0.12 μa. This was the error due to measuring the concentration for the polarographic reduction solutions. The i_D for each compound decreases somewhat as the "pH" is increased. The limiting currents (uncorrected for residual current) did not decrease with increasing "pH". Evidently, the decrease of i_D (corrected for residual current) is due to the increase of residual current at the more negative voltages.

The average limiting currents over the "pH" range are shown in Table XII. The experimental conditions which would affect the i_D or the terms of the Ilkovic Equation (6) were held constant for the compounds in Table XII. The diffusion coefficients were calculated using the Ilkovic equation. The value of $m^{2/3} t^{1/6}$ was obtained from Fig. 3 at the potential of the limiting current. The average diffusion coefficients over the "pH" range are given in Table XII.

TABLE XII

AVERAGE LIMITING CURRENTS AND DIFFUSION COEFFICIENTS OVER THE "pH" RANGE 1.5 TO 13.5

	i_D, μa.	$D \times 10^6$ ($\pm 0.2 \times 10^{-6}$), sq.cm./sec.	M.W.
Benzil	2.240	3.767	210
m-Anisil	1.994	2.971	270
p-Anisil	1.966	2.902	270
m,m'-Dihydroxybenzil	1.789	2.412	242
p,p'-Dihydroxybenzil	1.762	2.379	242
Vanillil	1.723	2.270	302
Syringil	1.691	2.172	362

The diffusion coefficients decrease with increasing molecular weight as one would predict, except for the dihydroxybenzils. The diffusion coefficients indicate that the migration of dihydroxybenzil is slowed down, probably due to a

solvent interaction. These compounds are capable of hydrogen bonding with the solvent which could exert a drag on the diffusion toward the electrode. Vanillil and syringil are capable of intramolecular hydrogen bonding (9), and, therefore, most of the hydrogen bonding ability of these compounds is consumed. This would explain why the i_D's and diffusion coefficients of vanillil and syringil are not significantly different from those of the dihydroxybenzils.

EFFECT ON THE HALF-WAVE POTENTIAL

The least squares method was used to obtain Fig. 9 and 10 showing the effect of "pH" upon the $E_{1/2}$. The data of Table XI were used for the calculations. The correlation coefficients of the least squares calculations were 0.995 or greater. One per cent confidence limits were obtained for all the correlations.

The data points of Table XI are represented by circles. The data points at "pH" 11.3 were not used in the least squares calculations and are represented by (X's) on Fig. 9 and 10. These data points do not fit the linear relationships. The rate of equilibration of the bicarbonate buffer system was too slow compared to the electrode reaction, and the "pH" at the DME was greater than 11.3 during the reductions (44).

The $E_{1/2}$ vs. "pH" relationship of vanillil was included in Fig. 9 to demonstrate the different "pH" dependence of hydroxy-substituted compounds. The data for benzil were included in Fig. 10 also for comparison.

The change of the "pH" dependence of $E_{1/2}$ between acid and basic media is due to a change in the role of the hydrogen ion in the reduction. It does not indicate a change in the over-all reaction since benzoin, p-anisoin, and vanilloin were the reduction products over the entire "pH" range. The proton could

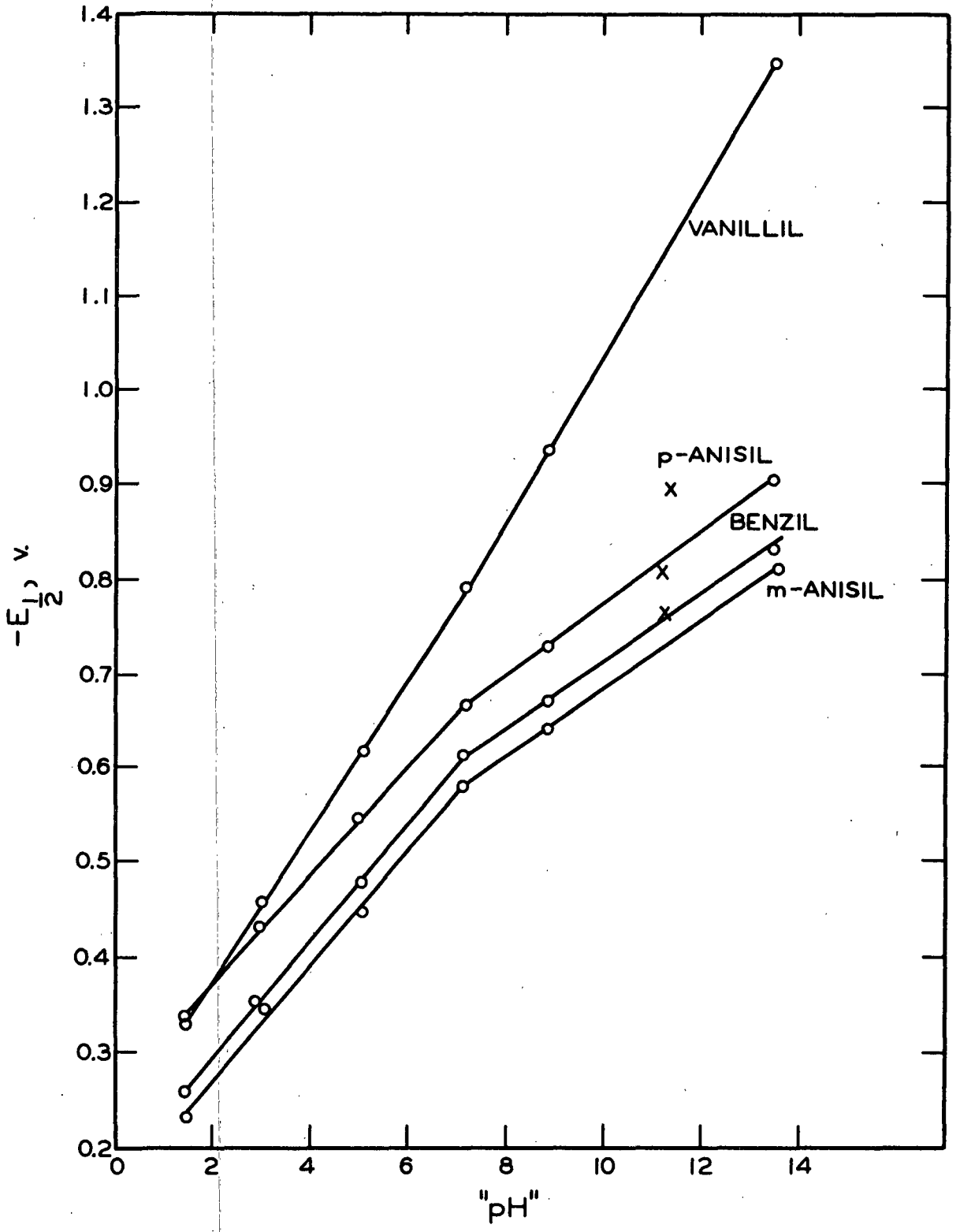


Figure 9. $E_{1/2}$ vs. "pH"

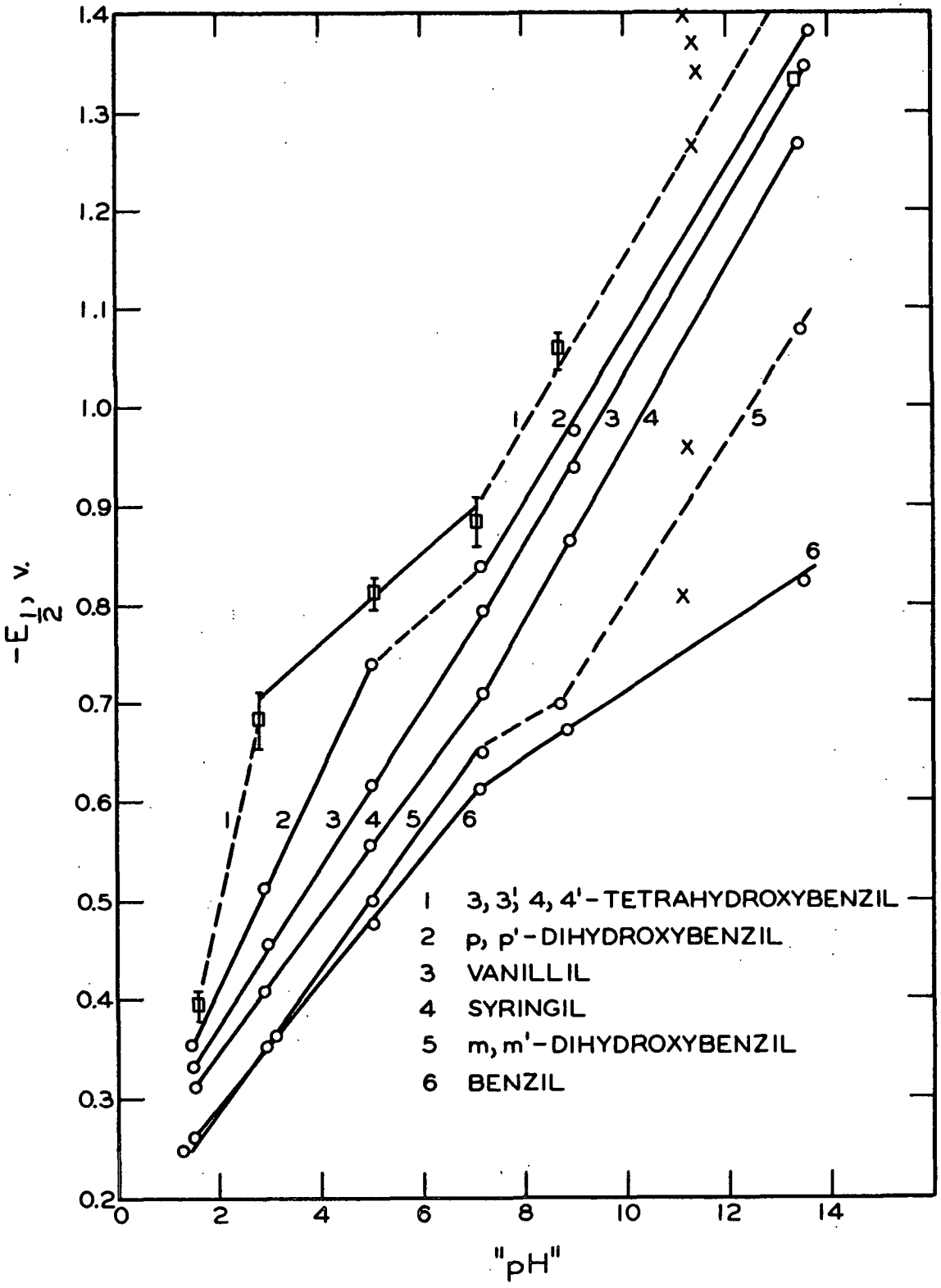


Figure 10. $E_{1/2}$ vs. "pH". 1. 3,3',4,4'-Tetrahydroxybenzil; 2. p,p'-Dihydroxybenzil; 3. Vanillil; 4. Syringil; 5. m,m'-Dihydroxybenzil; 6. Benzil

be transferred before the electron, preprotonation, in the acid region, while in the basic region, the proton and electron could be transferred at the same time.

The $E_{1/2}$'s of benzil, m-anisil, and p-anisil are dependent upon "pH" in both the acid and basic solutions. They are more "pH" dependent in the acid media than in the basic media. Chodkowska and Grabowski (13) also reported this type "pH" dependence for benzil. The change in slope occurred at pH 6.9 in their study as compared to 7.2 in this investigation. They used 48% ethanol by volume and the slightly different solvent system could account for the above difference.

The "pH" dependence of the $E_{1/2}$'s of the hydroxy-substituted compounds are shown in Fig. 10. The averaged data for 3,3',4,4'-tetrahydroxybenzil are represented by squares, and the lines through the squares represent the deviations of the individual data from the average. The dotted lines through two data points represent the expected linear relationships. m,m'-Dihydroxybenzil, syringil, and vanillil have linear relationships from "pH" 1.5 to 7.2. p,p'-Dihydroxybenzil has a straight-line relationship between "pH's" 1.5 and 5.0.

The hydroxy-substituted compounds are more "pH" dependent than benzil, m-anisil, and p-anisil at all "pH's" as seen from Fig. 9 and 10. The slopes of the $E_{1/2}$ vs. "pH" plots in acidic media increase in the order: nonhydroxy-substituted compounds < syringil < m,m'-dihydroxybenzil < vanillil < p,p'-dihydroxybenzil. The increase in slope parallels the increase of acidity determined from the potentiometric titrations (Table III, p. 32) with the exception of syringil and m,m'-dihydroxybenzil. The enhanced "pH" dependence of the hydroxy-substituted benzils is probably due to the solvent interactions with the hydroxyl groups. The hydroxyl groups on syringil are sterically hindered by the methoxyl groups, and may be shielded from solvent-solute interactions. The solvent-solute interactions apparently increase as the "pH" increases.

An interesting point of Fig. 10 is the straight line $E_{1/2}$ vs. "pH" relationship of m,m'-dihydroxybenzil crossing that of benzil. In terms of electron-withdrawing and electron-releasing ability, the m-hydroxy-substituent is an electron-withdrawer at "pH" 1.5 and becomes an electron-releaser as the "pH" is increased.

The $E_{1/2}$'s of the hydroxy-substituted compounds have a similar "pH" dependence in the basic media. The similar slopes of the $E_{1/2}$ vs. "pH" relationships indicate that the solvent-solute interactions on these compounds are identical in basic media. This was not the case for the reductions in acidic media.

In order to have similar solvent interactions, the solvent must act upon similar reducible species. The potentiometric titrations indicated that only the nonionized and the divalent forms of the hydroxy-substituted compounds were present in basic media. Therefore, the ionized form of these compounds must be the species which is reduced at the electrode. If this were not the case, the $E_{1/2}$ vs. "pH" relationships of the hydroxy-substituted compounds would vary in the basic media as they do in the acidic media.

The following reasons support the fact that the ionized forms of the hydroxy-substituted compounds are being reduced:

1. If both the nonionized and ionized forms were being reduced, one would expect two polarographic waves in the "pH" region 7 to 9. Müller and Baumberger (76) found this for the reduction to pyruvic acid in the intermediate pH region. The sum of the i_D's of the two waves equalled the i_D in the more acidic and basic solutions. In this investigation only one polarographic wave was produced at "pH's" 7 and 9.

2. The nonionized and ionized forms could be reduced at potentials less than 0.15 volt apart, and then only one wave would be produced. The i_D of this wave would be the same as that observed. If this were the case, there would not be a straight-line relationship between "pH's" 7.2, 9.0, and 13.5. There would be a change in slope between "pH" 9 and 13.5 indicating that only the ionized species was reduced at "pH" 13.5.

One might argue that the data at "pH" 11.3 are true phenomena and they represent the discontinuous $E_{1/2}$ vs. "pH" effect one would expect if the nonionized form were being reduced. Two obvious facts eliminate this possibility. (A) The $E_{1/2}$'s at "pH" 11.3 for benzil, m-anisil, and p-anisil would be included in the straight-line relationships for these compounds if the carbonate buffer system at "pH" 11.3 was adequate. There was no indication of ionization of benzil and p-anisil from potentiometric titrations. Also, Chodkowska and Grabowski (13) showed a straight-line relationship for benzil through pH's 7.5, 8.0, 9.5, 9.9, 11.7, 13.1, and 14.0. (B) The $E_{1/2}$ vs. "pH" data at "pH's" 7.2, 9.0, and 13.5 define least squares straight lines having correlation coefficients with 1% confidence limits. It is unlikely that this good correlation would occur by chance.

3. The slopes of the $E_{1/2}$'s vs. "pH" relationships are greater in the basic region than in the acidic region for m,m'-dihydroxybenzil, syringil, and vanillil. If the nonionized forms were reduced, one would expect these slopes to be less in the basic region, and similar to those for the nonhydroxy-substituted compounds. The line drawn between two data points, dotted lines for m,m'- and p,p'-dihydroxybenzil, and the line through the data

points at "pH's" 2.8, 5.1, and 7.1 for tetrahydroxybenzil (Fig. 10) represent the type of "pH" dependence one would expect if the nonionized forms were reduced. The slopes of these "straight lines" are similar to the slopes for the "pH" dependence of benzil, m-anisil, and p-anisil in the basic media.

4. Elving (55) has discussed a pH invariant region for the reduction of maleic and fumaric acids. For these acids, a split wave phenomenon occurs around pH 6. This is due to the rate of acid-anion interconversion being slow enough to permit the waves of both the acid and the corresponding, but more difficultly reducible anion to be simultaneously observed. In Fig. 10, "pH" invariant regions are shown for m,m'-dihydroxybenzil between 7.2 and 8.8, for p,p'-dihydroxybenzil between 5 and 7.2, and for tetrahydroxybenzil between 2.8 and 7.1. The "pH" of the invariant region becomes lower as the acidity of the acids increase. There was a slight indication of two waves for the reduction of tetrahydroxybenzil at "pH" 2.8. However, it cannot be ascertained if this behavior is due to an acid-anion equilibrium or the possibility of two one-electron processes which can be slightly distinguished due to the high electron-releasing ability of the four-hydroxy-substituents.

There appears to be little or no "pH" invariant region for syringil and vanillil. Intramolecular hydrogen-bonding (9) probably accounts for this phenomena. In other words, the hydrogens of the hydroxyl groups are stabilized by intramolecular hydrogen bonding with the methoxyl substituents. When a high enough "pH" is obtained for ionization, the hydrogens are pulled away. The

stabilizing influence of intramolecular hydrogen-bonding makes the "pH" range of a slow acid-anion equilibrium small compared to m,m'-, p,p'-, and tetrahydroxybenzil.

5. Elving, et al. (77) studied the effect of ionic strength on α-bromo-n-butyric acid over the pH range 1 to 12. They found the $E_{1/2}$ became more negative when the ionic strength was varied at pH's lower than 4.8. Variation of ionic strength at pH's greater than 4.8, caused the $E_{1/2}$ to become more positive. At the higher pH's the acid was ionized. The $E_{1/2}$'s of vanillil at "pH" 11.3 became more positive as the ionic strength was increased by adding potassium chloride. The $E_{1/2}$'s were -1.342, -1.301, and -1.271 for ionic strengths of 0.4, 0.5, and 0.6. The "pH" was not affected by the addition of the potassium chloride. The more positive values of $E_{1/2}$ as the ionic strength is increased indicates that an ionic species is being reduced.

The dissociation equilibria of these hydroxy-substituted benzils must be fast compared to the electrode reaction. If this were not the case, the reduction waves in the intermediate "pH" region would not have limiting currents similar to the acid and more basic regions. Also, there would be two waves and the limiting currents of these waves would be controlled kinetically by the ionization equilibria as is the case for pyruvic acid (78).

EFFECT OF STRUCTURE ON THE HALF-WAVE POTENTIAL

Structural effects are generally excellent criteria for evaluating a mechanism. A change in molecular structure had a marked effect on the 1,2-dicarbonyl

reduction site. The $E_{1/2}$ became more negative as the electron-releasing ability of the substituents increased. This is the expected shift, since the electron density around the reduction site is enhanced and makes the addition of electrons more difficult.

The expected order of ease of reducibility in acidic media, based on resonance and inductive effects, is m,m'-dihydroxybenzil, m-anisil, benzil, syringil, vanillil, p-anisil, p,p'-dihydroxybenzil, and 3,3',4,4'-tetrahydroxybenzil. The observed order at "pH" 1.5 (Table XI) is identical to the above with the exception of m,m'-dihydroxybenzil and m-anisil. In less acidic solutions the observed order changes. m,m'-Dihydroxybenzil changes from an electron-withdrawer to an electron-releaser. At "pH" 3.0, vanillil is harder to reduce than p-anisil, and at "pH" 5.0, both vanillil and syringil are harder to reduce than p-anisil. At "pH" 5.0 the observed order of ease of reduction is m-anisil, benzil, m,m'-dihydroxybenzil, p-anisil, syringil, vanillil, p,p'-dihydroxybenzil, and tetrahydroxybenzil. These changes in the ease of reduction could be due to solvent-solute interactions which alter the electron density around the reduction site.

The expected order of ease of reducibility in basic media is somewhat changed due to the ionization of the hydroxy-substituents. The order is m-anisil, benzil, p-anisil, m,m'-dihydroxybenzil, syringil, vanillil, p,p'-dihydroxybenzil, and tetrahydroxybenzil. This is the observed order in the basic media with two exceptions (see Table XI). (1) At "pH" 9.0, m,m'-dihydroxybenzil is easier to reduce than p-anisil. This is due to the small degree of ionization of m,m'-dihydroxybenzil at this "pH". (2) Tetrahydroxybenzil is easier to reduce than vanillil and syringil at "pH" 13.5. If the change of ultraviolet absorption spectrum at "pH" 13.5 (Table IV) was caused by the ionization of the m-hydroxyl groups, one would expect the reduction of tetrahydroxybenzil to be more difficult than vanillil and syringil. Since this is not the

case, the odd behavior of this compound at "pH" 13.5 could be due to some chemical reaction or rearrangement.

CORRELATION OF HALF-WAVE POTENTIALS

The effect of substituents on the $\underline{E}_{1/2}$ has just been discussed qualitatively in terms of the electron-withdrawing and releasing ability of the substituents. A quantitative correlation of reactivity, as measured by the $\underline{E}_{1/2}$, and structure would enable the $\underline{E}_{1/2}$'s for any substituted benzil to be predicted.

The Hammett Equation (4a) is a linear free energy equation which has been used very successfully for quantitative correlations of reactivity and structure. The $\underline{E}_{1/2}$ potentials for reversible electrode reactions are related in a simple way to the free energy change of a reaction. Many investigators have found good correlations between polarographic data and structure using the Hammett sigma (σ) values.

Attempts to correlate the $\underline{E}_{1/2}$'s obtained in this investigation using the following Hammett Equation were not very successful.

$$E_{1/2} - E^{\circ}_{1/2} = \frac{0.0591}{\alpha n} \rho \sigma \qquad (14)$$

where

$\underline{E}^{\circ}_{1/2}$ = half-wave potential of the unsubstituted compound, benzil

$\underline{E}_{1/2}$ = half-wave potential of a compound substituted at the meta- or para-position

σ = Hammett substituent constant

ρ = Hammett reaction constant

Plots of $(\underline{E}_{1/2} - \underline{E}^{\circ}_{1/2})$ vs. sigma are shown in Fig. 11 for "pH's" 1.5, 3.0, and 5.0. The solid lines are the least squares lines calculated from the data points for the compounds shown in Fig. 11. The broken lines for "pH's" 3.0 and

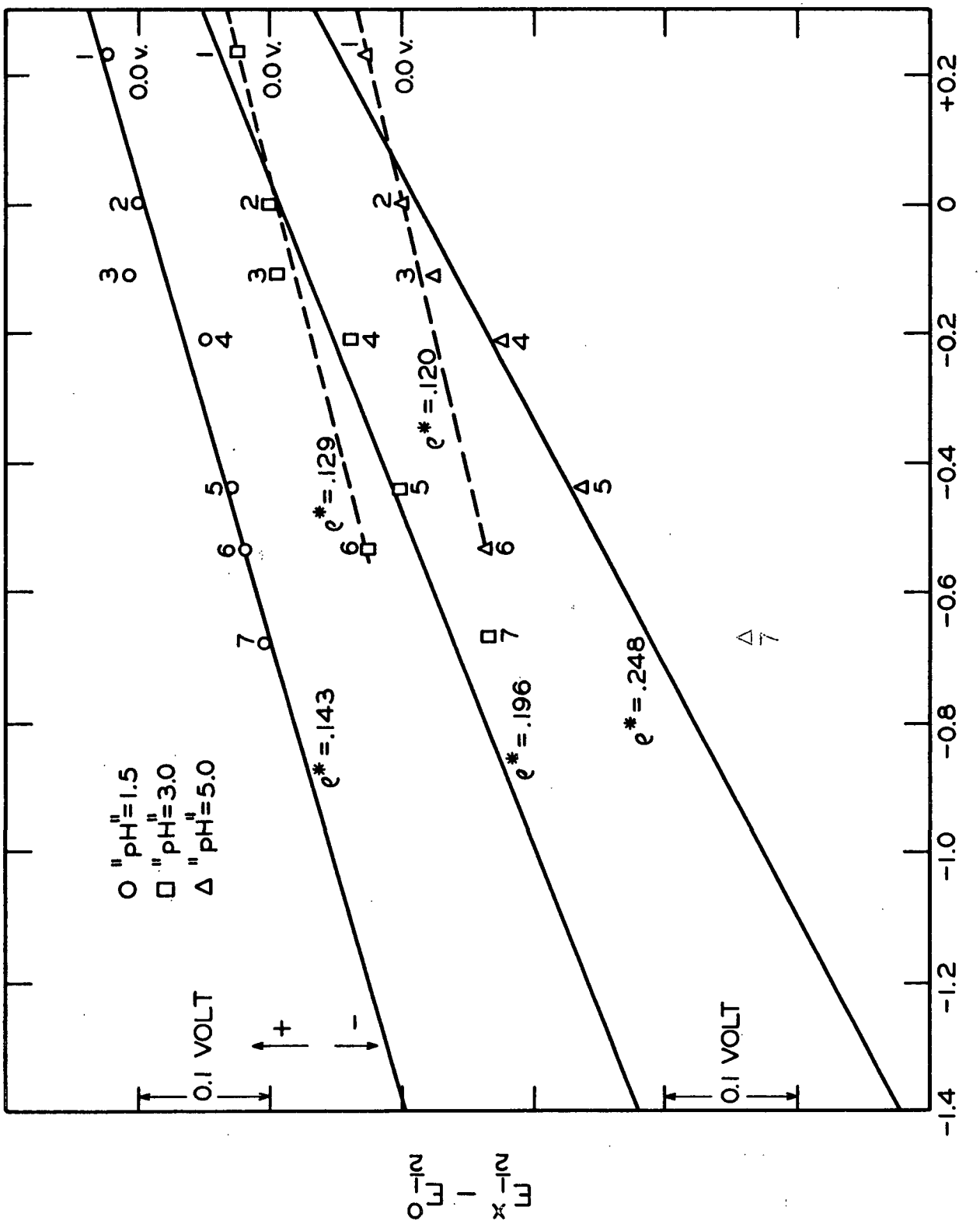


Figure 11. Hammett Correlations in Acid Media. 1. m-Anisil; 2. Benzil; 3. m,m'-Dihydroxybenzil; 4. Syringil; 5. Vanillil; 6. p-Anisil; 7. p,p'-Dihydroxybenzil

5.0 are the least squares fit for the data of m-anisil, benzil, and p-anisil. These three compounds produced Hammett correlations at all "pH's". The correlation including the hydroxy-substituted compounds decreases as the "pH" is increased. There was no correlation between all the compounds in the basic media. The hydroxy sigma values used in Fig. 11 were reported by Bright and Briscoe (79) for a 50% ethanol-water solvent ($\sigma_{p\text{-}OH} = -0.335$, $\sigma_{m\text{-}OH} = -0.055$). All other values are reported by Hine (4a) based on the ionization of benzoic acids. The sigma values for each compound were calculated by assuming that the substituent effects on both benzene rings were additive. This procedure was used, since it has been shown that both the carbonyl groups are reduced, pages 40 to 43. The (ρ^*) values are the slopes of the lines and ρ^* equals $(0.0591/\alpha n)\rho$. The actual ρ value cannot be calculated since the αn values vary from compound to compound even at the same "pH". However, at "pH" 1.5 using $\alpha n = 1$, ρ equals +2.6.

The failure of the Hammett Equation to correlate the hydroxy-substituted compounds is due to the irreversibility of the electrode process and solvent interaction with the hydroxy substituents. Any substituent effects other than induction and resonance, such as steric hindrance or solvent interactions, will cause most Hammett correlations to fail unless the effect is constant for the whole series of compounds.

An attempt was made to correct for the ionization of the hydroxy substituents by calculating the degree of ionization from potentiometric titrations. A continuous sigma value for the ionized hydroxyl group was calculated from a force-fitted sigma value using p,p'-dihydroxybenzil at "pH" 11.0 where the hydroxyl group was completely ionized. The continuous sigma value was used to calculate the sigma values for p,p'-dihydroxybenzil and the other hydroxy-substituted

compounds at different "pH's". The correlation was not improved. This indicates there are solvent effects or interactions other than ionization and that these effects are different for each compound.

The $E_{1/2}$ for an irreversible process is dependent upon αn, the rate constant, the diffusion coefficient, and the drop time as shown in Equation (10). It follows that any correlation of $E_{1/2}$ and σ can only be valid when all these quantities are comparable for the series of compounds. Tables VII, X, XII, and Fig. 3 show how these quantities vary with "pH" and the different compounds. The variations of the above quantities, except the diffusion coefficients, are less around the potential of the ECM. Therefore, the $E_{1/2}$ vs. σ correlation should be better at "pH" 1.5, since the reduction potentials are closer to the ECM. This is the case. As the "pH" is increased, the reduction potential becomes more negative, the variation of the above quantities increases, the solvent interactions increase, and electrostatic repulsions of reducible species at the double layer of the electrode (58, 60, 80) make the electrode reduction more complicated. Attempts were made to correct the $E_{1/2}$ for some of these effects in order to obtain a better correlation at higher "pH's". However, as indicated from the kinetic data, these effects are too complicated to be isolated by using the data obtained in this investigation with the existing theory.

An examination of the data shows that the reversibilities for benzil, m-anisil, and p-anisil are similar. Figure 12 is a Hammett plot of $(E^{x}_{1/2} - E^{o}_{1/2})$ vs. σ for these compounds at "pH" 5.0. The $E_{1/2}$'s shown in Table XIII were calculated from this figure by determining the $(E^{x}_{1/2} - E^{o}_{1/2})$ value for the respective σ and then adding the $E_{1/2}$ of benzil obtained from Fig. 9 at the appropriate "pH". The observed $E_{1/2}$ for the compounds listed in Table XIII were obtained from Sobieski (81).

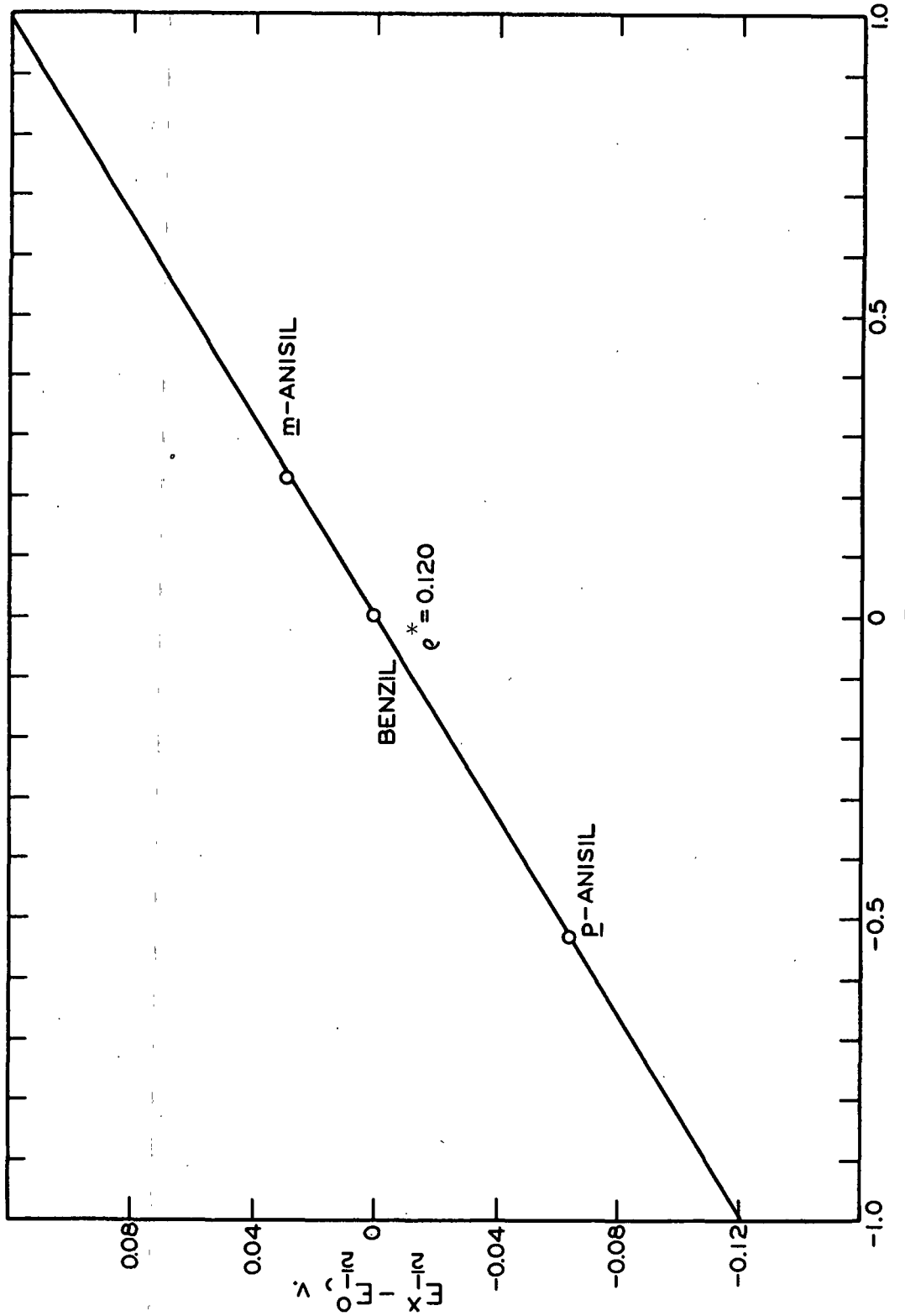


Figure 12. Hammett Correlation of Nonsubstituted Compounds, "pH" 5.0

TABLE XIII

CALCULATED HALF-WAVE POTENTIALS FOR SUBSTITUTED BENZILS $-E_{1/2}$ (VOLTS)

Substituted Benzil	"pH" 1.33		"pH" 5.6		"pH" 13.6	
	Calcd.	Exptl.[a]	Calcd.	Exptl.	Calcd.	Exptl.
m,m'-Dichloro-	0.160	0.163	0.422	0.401	0.753	0.766
m-Chloro-	0.204	0.200	0.466	0.443	0.797	0.793
p-Chloro-	0.220	0.210	0.484	0.456	0.815	0.805
m-Methoxy-	0.236	0.231	0.498	0.480	0.829	0.823
p-Methyl-	0.272	0.256	0.532	0.507	0.849	0.847
p-Methoxy-	0.282	0.271	0.544	0.532	0.875	0.863
p,p'-Dimethyl-	0.289	0.278	0.545	0.523	0.882	0.866
m-Hydroxy-	0.256	0.238	0.518	0.500	0.849	0.900
p-Hydroxy-	0.290	0.278	0.546	0.593	0.883	1.045
p-Nitro-	0.165	0.039	0.427	0.276	0.758	0.432
p-Dimethylamino-	0.150	0.223	0.412	0.566	0.743	0.916

[a]These experimental data were obtained in a 50% ethanol-water solvent by Sobieski (81). A different capillary was used, but the characteristics of that capillary and the one used in this investigation were similar.

The calculated values agree with the experimental values at "pH's" 1.33 and 13.6 (within experimental error) for the first seven compounds. The on values have less variation around the ECM, as discussed earlier, and the reductions at "pH" 13.6 are reversible or approach reversibility. Therefore, the agreement at these "pH's" would be expected. The agreement between calculated and experimental values is better for the electron-withdrawing substituents (chloro- and m-methoxy-) than for the electron-releasing substituents (p-methoxy- and methyl-).

The variations between calculated and experimental data at "pH" 5.6 are probably due to differences in reversibility. This emphasizes the effect of

reversibility on the Hammett correlation since Fig. 12 was plotted for data obtained at "pH" 5.

The agreement between calculated and experimental values for the last four compounds is poor. There are known solvent effects such as ionization and hydrogen-bonding for these compounds.

The data in this section indicate that the solvent interactions cause the Hammett equation to fail. It also is evident that the solvent interactions in conjunction with the electron-releasing substituents are causing the increased irreversibility of the hydroxy-substituted compounds. Other interactions between the reducible species and the dropping mercury electrode such as electrostatic repulsions and electric field induced ionizations could be involved.

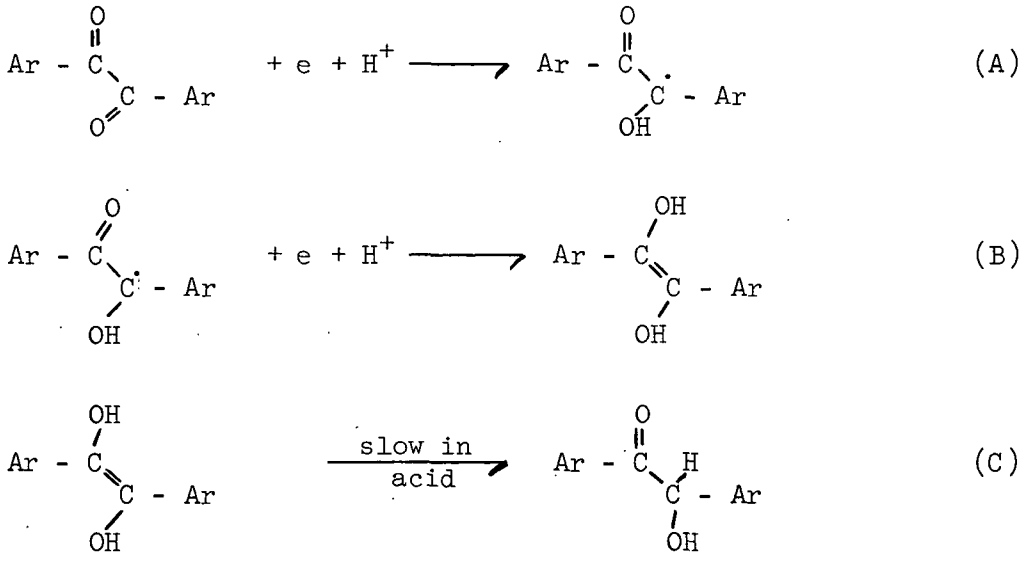
DISCUSSION

The polarographic reductions of benzil and the benzil derivatives are two-electron processes over the "pH" range investigated. The reductions are dependent upon the hydrogen-ion concentration. The role of the hydrogen-ion in the reduction is different in acid and basic media. The reductions become more reversible as the "pH" increases and benzil, m-anisil, and p-anisil are reversible reductions in the very basic solutions. The kinetic analyses indicate more than one irreversible process. The reduction product of the first wave is the enediol form of benzoin. In acid solutions the enediol rearranges slowly to the keto form. This rearrangement is facilitated by alkali and is faster in the basic solutions.

Although the experimental evidence does not clearly indicate the nature of the first wave (for example, if the electrons are transferred separately or

simultaneously) the following mechanism is proposed for the nonhydroxy substituted compounds.

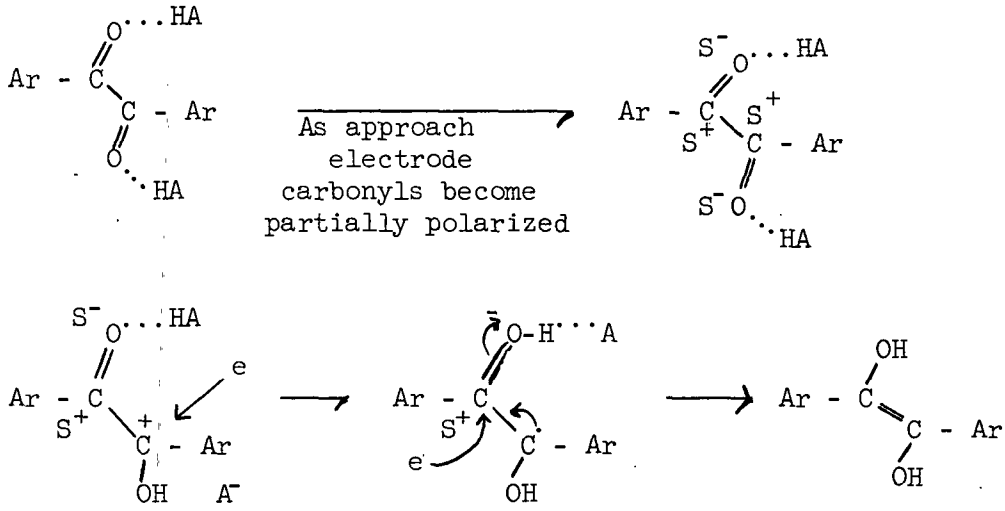
In acid solutions one or both of the carbonyl groups are preprotonated under the influence of the electric field at the electrode. The α_n values indicate that one electron is required for the rate-determining process. One can assume a stepwise process



in which Steps (A) and (C) are both irreversible.* The kinetic analysis only indicates that there is more than one rate-determining step. The exact number cannot be ascertained. The proton and electron are not transferred simultaneously in Steps (A) and (B). The proton is transferred first, especially at low "pH's", and immediately afterward the electron is transferred. This could be termed "preprotonation," but the proton is not transferred until the reducible species is influenced by the electric field (double layer) of the electrode. At "pH"

*Benzil is written in the trans- form. A molecular model of benzil showed the ortho hydrogens overlapped when the planer-cis- form was made. The cis- form can exist, but then the two benzene rings are not in the same plane.

1.5, the protonation is aided by hydrogen bonding between the carbonyl groups and the acid.



These proposed intermediate steps are consecutive and are too fast for the electrode to distinguish. The first electron transfer facilitates the polarization of the second carbonyl so that the transfer of the second electron is faster than the first. This type of hydrogen-bonding is used to explain the acid-catalyzed mechanism for halogenation of ketones (82). Kuhn (83) observed this type of hydrogen-bonding when dry hydrochloric acid was added to tetramethylene glycol.

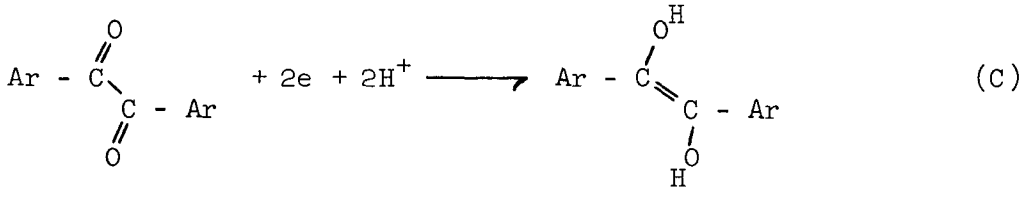
At higher "pH's" the polarization of the carbonyl group is aided less by hydrogen bonding with acid. A greater potential is required to cause polarization and subsequent electron transfer. Therefore, the $E_{1/2}$ increases.

In basic media, the dependence of the reduction on "pH" is decreased, since the proton concentration is too small to aid in "preprotonation." The electric field must supply all the energy to polarize the carbonyl groups. The electric field also has to attract protons to the electrode. The smaller the concentration

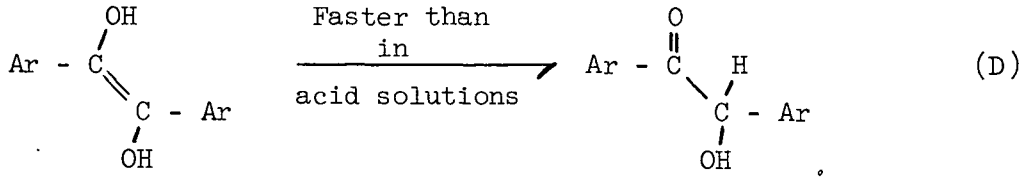
of protons, the more energy required to attract them to the electrode. Therefore, the reduction potential becomes more negative with increasing "pH".

The carbonyl groups are influenced equally at the more negative potentials and, consequently, the rate of successive transfer of the two electrons is more rapid. In the very basic region the two electrons are transferred simultaneously.

In the intermediate pH region the αn values indicate that almost two electrons are required for the rate-determining process. The following stepwise process may be assumed.



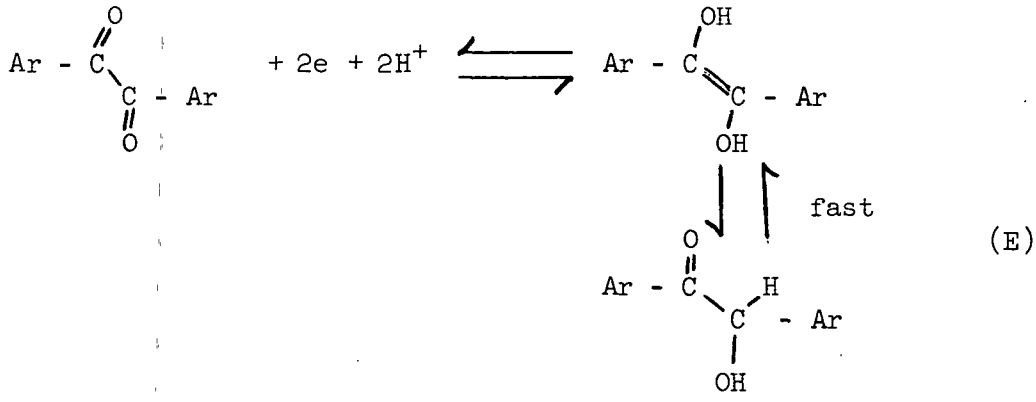
(C)



(D)

The enediol-keto rearrangement at these "pH's" is probably influencing the reversibility to a greater extent than the electron and proton transfer. However, Step (C) cannot be entirely reversible at these "pH's" since there is an indication of more than one irreversible process.

In very basic media, the αn data and kinetic analyses indicate a reversible two-electron process.



(E)

The enediol to benzoin rearrangement is fast. Therefore, the reduction is reversible. The protons could be transferred simultaneously or just after the electrons are transferred. Since the data at "pH" 13.5 form a linear relationship with the data at "pH's" 7.2 and 9.0, Mechanism (E) was chosen.

Benzil, m-anisil, and p-anisil are not affected by solvent interactions. Their reduction potentials are influenced by the ease of protonation, and the electron-withdrawing and electron-releasing ability of the substituents. The reductions of hydroxy-substituted compounds are influenced by hydrogen bonding and ionization in addition to the influences stated above. Therefore, the reductions of these compounds are more "pH" dependent.

The effect of pH on hydrogen-bonding is not understood. One investigation showed that the infrared frequency of three alcohols (ethyl, methyl, and benzyl) increased with decreasing acidity (84).

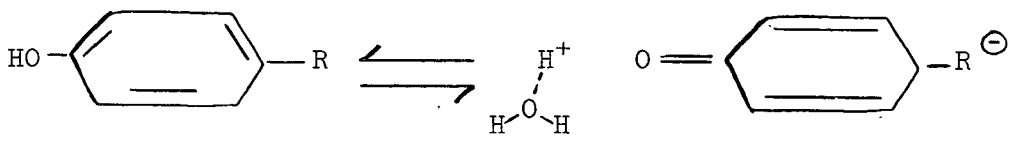
The Hammett correlation indicated the hydrogen-ion affects all compounds equally at "pH" 1.5. The hydrogen-bonding or "preprotonation" at the carbonyl groups must be more important than hydrogen-bonding at the hydroxyl groups. As the "pH" is increased, the ease of protonation decreases, and hydrogen-bonding at the hydroxyl groups becomes more important. This hydrogen-bonding enhances the electron-releasing ability of the hydroxyl groups and causes the electron

density around the reduction site to increase. A greater electric field is needed to polarize the carbonyl group and, therefore, the reduction potentials of the hydroxy-substituted compounds are greater than one would predict from only electron-withdrawing and electron-releasing considerations. The larger slopes of the $E_{1/2}$ vs. "pH" relationships for these compounds are evidence for this type of phenomenon. This also explains why the m-hydroxy substituent changes from an electron-withdrawer to an electron-releaser as the "pH" is increased.

Peover and Davies (85) studied the influence of hydrogen-bonding on the polarographic reduction of p-benzoquinones. Their data indicated that the reduction potential became more negative as the hydrogen bonding ability between solvent and reducible species increased.

The electron-releasing ability of vanillil and syringil is not enhanced as much as that of p,p'-dihydroxybenzil. The solvent-solute hydrogen-bonding capacity of these compounds is decreased by intramolecular hydrogen-bonding with the methoxyl groups. The hydroxyl groups of syringil also could be sterically hindered. Although p-anisil has a greater electron-releasing ability than vanillil and syringil, these compounds are harder to reduce than p-anisil above "pH" 3 and 5, respectively.

de la Mare, et al. (86) suggest that due to hyperconjugation, hydroxyl substituents in acidic media have an advantage over methoxyl substituents in electron-releasing ability. Eaborn and Webster (87) also suggested the same phenomenon and considered the solvent to assist this effect by hydrogen-bonding.



This phenomenon could increase the electron-releasing ability of p,p'-dihydroxybenzil and tetrahydroxybenzil, and make their $E_{1/2}$'s more negative.

3,3',4,4'-Tetrahydroxybenzil also is capable of intramolecular hydrogen bonding. This decreases the electron density around the free hydroxyl group and makes it easier to ionize. The electron density around the reduction site is then increased, and the reduction potential becomes more negative.

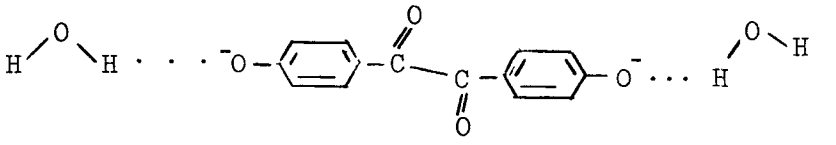
As the "pH" is increased the hydroxyl groups begin to ionize. The reducible species pass through the "pH" invariant region, as discussed earlier, and in the intermediate and more basic regions the ionized forms of the hydroxy-substituted compounds are reduced.

Evidence for the reduction of the ionized forms (in the intermediate basic region) in preference to the supposedly, easier reducible nonionized forms of the hydroxy-substituted compounds was discussed earlier. At present three possibilities for this unexpected phenomenon come to mind.

There is a possibility of ion-pair formation between the di-anion of the reducible species and the cations of the buffer salts or supporting electrolytes. The ion-pair would decrease the electron-releasing ability of the negatively charged oxygen atom and decrease the electron density around the reduction site. Hine (88) states that in 0.01N aqueous solutions (or less), most salts are completely dissociated. The concentration of salts in the buffer solutions were at least 0.06M, and the ionic strength was 0.2 in this investigation. Although ion-pair formation is a possibility, it does not seem likely that it alone could account for the observed phenomenon.

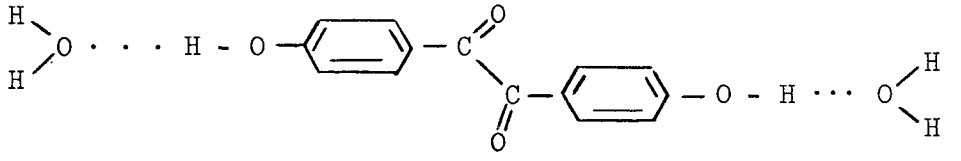
The ionized form has a different capacity for hydrogen bonding than does the nonionized form. Gordy and Stanford (89) have shown by measuring infrared

frequencies, that the more basic the hydrogen acceptor the stronger are the hydrogen bonds. The solvent-solute hydrogen bonds of the ionized species should be stronger than those of the nonionized species. Also, the hydrogen bonds with the ionized species would decrease the electron-releasing capacity of the ionized hydroxyl groups.



shift of electron density shift of electron density

The hydrogen bonds with the nonionized species enhance the electron-releasing capacity of the nonionized hydroxyl groups.



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Actually this explanation is very similar to the ion-pair formation. A quantitative estimate of the influence of the two types of hydrogen bonding is difficult. It does seem unlikely, however, that the anion-hydrogen-bonding could totally eliminate the larger electron releasing ability of an ionized hydroxyl- vs. the nonionized hydroxyl substituent.

The third possibility involves the influence of the electric field on the reducible species as it approaches the electrode. The electrostatic attraction of the negative electrode for positive ions could be great enough to ionize all the reducible species before the reduction occurs. This would mean that the ionization is more dependent upon electrode potential, than upon the "pH" of

the solution. However, the "pH" must be high enough so that the demand for protons at the electrode is greater than the concentration in the solvent-buffer system.

Earlier it was shown (p. 71) that the ionization was more complicated than just a chemical acid-base reaction. This was evident when a continuous sigma value for the hydroxyl ionization could not be obtained from the potentiometric titrations. This possibility for ionization could be one of the complications causing the failure of a reactivity-structure correlation.

It now becomes apparent that the solvent interactions of hydrogen bonding and ionization are dependent upon the electrode potential as well as the "pH" of the solution. The mechanism at "pH" 1.5 with protonation as the rate-determining step is probably correct for all compounds, since a good Hammett correlation was obtained at this "pH". The over-all reaction at other "pH's" also is correct for all compounds, since benzoin, p-anisoin, and vanilloin were isolated as the reduction products.

Any statements concerning the irreversible steps of the hydroxy-substituted compounds at other "pH's" would be pure speculation. A thorough kinetic study using alternating current and oscillographic polarographic techniques should be the next step to increase our knowledge of these electrode reductions.

ACKNOWLEDGMENTS

The author sincerely appreciates the advice and assistance of his thesis committee, Drs. I. A. Pearl, D. C. Johnson, and D. D. Bump. The time, advice, and equipment contributed by others on the Institute staff was also appreciated.

The author would like to express thanks to the following: the members of the lignin chemistry department for supplying many of the organic compounds; Mr. L. O. Sell for the ultraviolet and infrared analyses; and Mr. J. F. Sobieski for many helpful discussions and for the use of data he has obtained in a similar investigation.

The author wishes to express sincere thanks and appreciation to his fiancee, Miss Patricia J. Verhagen, for typing and proofreading, and her continual encouragement throughout the course of this work.

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